Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplemenatry Information for

New Molecularly Engineered Binuclear Ruthenium (II) Complexes for Highly Efficient Near-Infrared Light-Emitting Electrochemical Cell (NIR-LEC)

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Contents of supplemenatry Information

1. Methods and Materials

All reagents and solvents were purchased from commercialsources and used without further purification.NMR spectra were recorded on a Bruker 250 MHz spectrometer with $CDCl_3$, D_6-DMSO and tetramethylsilane (TMS) as solvent and internal reference, respectively .Elemental analyses were performed on Elementar Vario EL CHN elemental analyzer. TOF-Mass were performed on LC-MS/MS "Quattro Micro API micromass Waters 2695. Scanning electron microscope (SEM) was perform by TESCAN Vega Model. IR spectra were recorded on a Perkin-Elmer 597 spectrometer.The Electrochemical studies of ruthenium complexes (2×10^{-3}M) were performed under a dry N_2 atmosphere at 298 K by using SAMA500 potentiostat electrochemical analyzer with conventional three electrode cell, a Pt disk as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The CV measurements were performed at room temperature using 0.10 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte and degassed acetonitrile as the solvent. In CV the following parameters and relation were used: scan rate, 100 mV s^{-1}; formal potential $E^{o'} = (E_{pa} +/E_{pc})/2$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. The oxidation (E_{ox}) was used to calculate the HOMO/LUMO energy levels and electrochemical energy gap energy ($E_{gap\ Elc}$) using the equations E_{HOMO}=-(E_{ox}(vs.F_c/F_C^+)+ 4.8 eV), $E_{g\ Elc}$ = [$E_{1/2\ ox}$ - $E_{1/2\ red}$]V and E_{LUMO} = E_{HOMO} + $E_{g\ Elc}$ eV, which is the half-wave oxidation potential of ferrocene was found to be 0.43 V [1].The optical energy gap ($E_{g\ Opt}$) was calculated from the intersection of absorption and emission spectra in acetonitrile solution. UV–visible absorption spectra was recorded on an Ultrospec3100 pro spectrophotometer in acetonitrile solutions at 298 K . Photoluminescence (PL) emission spectra of ruthenium complexes in degassed solutions at 298 K was recorded using Varian-Cary Eclipse flourocence spectrophotometer. The PL and PLQYs in neat films were measured with an absolute PLQY measurement system (Hamamatsu C11347) equipped with an integrating sphere. The excited-state lifetime measurements were carried out on a HydraHarp Picoquant multichannel time correlator. Excitation was provided using a 405 Sepia picosecond diode laser delivering. pulses of less than 130 ps with 2 MHz repetition rate. Single wavelength detection was conducted with a thermo-electrically cooled Hamamatsu photomultiplier coupled to a 0.5mSP-2558 Princeton Instruments (Acton Research) spectrometer equipped with a 600 lines/mm grating.

The average lifetime is obtained after using bi-exponential decay model through the following equation (Eq. S1) :

$$\tau_{avg} = \sum_{i=1}^{n} \frac{A_i \tau_i^2}{A_i \tau_i}$$

where t τ_{avg}= average lifetime, A_i = amplitude of the components, τ_i = decay times of the component, n = no. of decay times. The PLQY (PL quantum yields) were calculated by comparison with $[Ru(bpy)_3]^{2+}$ in degassed CH_3CN solution at room temperature as a standard ($\emptyset_{std} = 0.095$) [2] using to the well-known following equation (Eq. S2):

$$\emptyset_{unk} = \emptyset_{std}.(\frac{I_{unk}/A_{unk}}{A_{std}/I_{std}}).(\frac{\eta_{unk}}{\eta_{std}})^2$$

In equation,Φ_{unk} is PL quantum yield of ruthenium complexes, I_{unk} and I_{std} are the integrated areas of the corrected PL spectra of the ruthenium complexes and standard respectively, A_{unk} and A_{std} are the absorbances of the ruthenium complexes and the standard at the excitation wavelength (λ_{exc}= 450 nm), and η_{unk} and η_{std} are the indexes of refraction of the respective solvents (taken to be equal to the neat solvents in both cases). Neat films of cationic ruthenium complexes (thickness of about 120 nm) for study of solid emission and lifetimes were obtained by spin-coating of spectrophotometric grade acetonitrile solution of complexes (5% (w/v)) on a quartz substrate at 1000 rpm for 25 s. After evaporation of the solvent in glove-box, the neat films were dried overnight under vacuum at room temperature.

Device fabrication and measurement : Indium tin oxide (ITO) coated glass with a sheet resistance of 15 Ω/square and size of 1.5 × 2.0 cm was used as the transparent anode. After being sufficiently cleaned by soaking in ultrasonicated isopropanol, aceton and deionized water, it was dried in the oven at 110°C for 2h. Thin films (ca. 35 nm) of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were spin-coated onto ITO/glass substrates at 1200 rpm for 60 s and then baked at 150 °C for 30 min in ambient air. The emissive layers (120 nm) of NIR LECs were spin-coated from a 5% (w/v) acetonitrile solution at 1000 rpm for 25 s . All solution and film preparation were performed under ambient conditions. After spin coating, the devices have been transferred to an inert atmosphere glove box (<0.1 ppm O_2 and H_2O) and heated in 70 ^oC for 5h to completely removed the solvent. Then, the Ag electrode (70 nm) was thermally vapor deposited and encapsulated into the glove-box. The thicknesses of the films have been measured with an Ambios XP-1 profilometer. The active area of the devices were 0.16 cm^2. All EL measurement were carried out in air atmosphere. The current density, luminescence versus the voltage and emission characteristics of LEC devices were measured using an AvaSpec-125 Fiber Optic spectrophotometer, a SAMA500 electroanalayzer system and a True Color Sensor MAZeT (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System.

2. Synthesis and characterization

The compounds cis-[Ru(dmbpy)$_2$Cl$_2$].2H_2O, cis-[Ru(bpy)$_2$Cl$_2$].2H_2O, and 1,10-phenanthroline-5,6-dione (phendione) were synthesized according to reference methods [3].

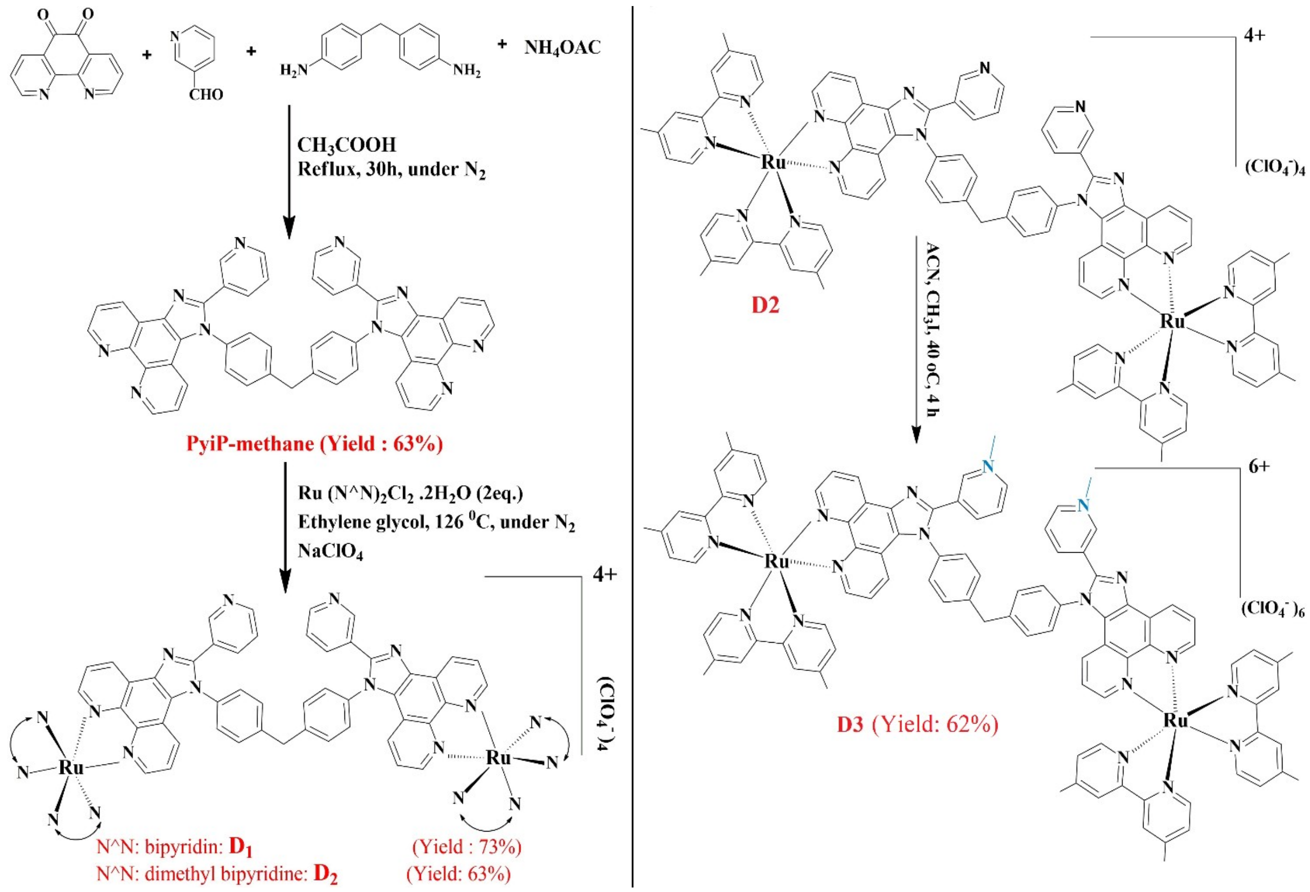
Synthesis of bis(4-(2-(pyridin-3-yl)-1H-imidazo[4,5-f][1,10]phenanthrolin-1-yl)phenyl) methane (PyiP-methane): After the 1,10-phenanthroline-5,6-dione (0.212 g, 1.0 mmol), was desolved in 12 ml glacial acetic acid, pyridine-3-carboxaldehyde (0.108 g, 1.0 mmol), 4,4'- diaminodiphenylmethane (0.99 g, 0.50 mmol) and ammonium acetate (770 mg, 10 mmol, excess) was added and the mixture refluxed for 30 h under N_2 atmosphere. The reaction mixture was cooled to room temperature, poured into 40 mL distilled water. The suspension mixture neutralized with aqueous ammonia solution (25%). The organic compound was extracted with 40 mL of chloroform and then removed the solvent by rotary evaporation and the residue was washed with ethanol and acetone. The recrystallization from CH_2Cl_2–acetone (1/5, v/v) was repeated one more time to obtained the product as a white powder. Yield: 63%. mp. 283°C, Anal. calcd. For $C_{49}H_{30}N_{10}$ (%): C, 77.56 ; H, 3.98; N, 18.46. Found (%): C, 77.58; H, 3.96; N, 18.42. IR (KBr): $\tilde{\nu} =$ 3059 (C-H aromatic), 2961 (C-H aliphatic), 1617 (C=C), 1608 (C=N), 1375 cm^{-1} .^{1}HNMR (250 MHz, $CDCl_3$): 9.19 (d, J = 5 Hz, 2H), 9.09 (d, J = 7.5 Hz, 2H), 9.03 (d, J = 5 Hz, 2H), 8.72 (s, 2H), 8.54 (d, J = 5 Hz, 2H), 8.06 (d, J = 7.5 Hz, 2H), 7.72-7.77 (m, 2H), 7.42-7.64 (m, 12H), 7.25 (m, 2H), 4.40 (s, 2H, Hydrogens of -CH_2- as alkyl spacer). ^{13}CNMR (62 MHz, $CDCl_3$): 149.92, 149.41, 149.16, 148.10, 145.01, 144.32, 142.68, 136.61, 136.03, 131.21, 130.46, 129.02, 127.84, 127.17, 126.27, 123.61, 123.22, 122.10, 119.56, 41.09 (Cabon of -CH_2- as alkyl spacer). TOF-MS (CH_3OH, m/z): 759.24 ([M+1])

General procedure for synthesis of D1 and D2, [Ru$_2$(N^N)$_4$(PyiP-methane)](ClO$_4$)$_4$: 0.1 mmmol of cis-[Ru(N^N)$_2$Cl$_2$].2H_2O and 0.05 mmol of PyiP-methane (39.2 mg) was added to 5 ml ethylene glycol and deggased by N_2 and heated under N_2 atmosphere at 126 °C for 18.0 h to give a clear red solution. After the mixture was cooled to room temperature, saturated aqueous solution of $NaClO_4$ was added drop by drop until gave a orange precipitate and washed several times with deionized water to remove traces rest of salts. The crude product was purified by column chromatography on alumina with acetonitril-toluene (3/1, v/v) as an eluent. The mainly red band was collected. The solvent was removed under reduced pressure and red solid were obtained.

[Ru$_2$(bpy)$_4$(PyiP-methane)](ClO$_4$)$_4$ (D1). Yield: 81%. IR (KBr): $\tilde{\nu} =$ 3091 (C-H aromatic), 2938 (C-H aliphatic), 1624 (C=C), 1597 (C=N), 1519, 1089 (ClO_4) cm^{-1}. ^{1}HNMR (250 MHz, D_6-DMSO): 9.21 (d, J = 7.5 Hz, 2H), 8.83 (m, 10H), 8.51 (s, 2H), 8.26-8.05 (m, 10H), 8.03-7.87 (d, J = 5 Hz, 6H), 7.86-7.73 (m, 8H), 7.69-7.45 (m, 16H), 7.43-7.29 (m, 6H), 4.44 (s, 2H, Hydrogens of -CH_2- as alkyl spacer). ^{13}CNMR (62 MHz, D_6-DMSO): 157.13, 157.00, 151.83, 151.27, 150.95, 150.55, 146.06, 145.81, 144.45, 138.41, 137.01, 136.70, 134.76, 131.59, 131.03, 129.40, 128.50, 128.37, 128.18, 127.51, 126.22, 125.93, 124.95, 123.10, 121.86, (^{13}C Signal of -CH_2- as alkyl spacer is buried under D_6-DMSO peak at 39-41 ppm). Anal. calcd. For $C_{89}H_{62}Cl_4N_{18}O_{16}Ru_2$ (%): C, 53.89; H, 3.15; N, 12.71. Found (%): C, 53.88; H, 3.16; N, 12.71. TOF-MS (CH_3OH, m/z): 892.04 ($[D1\text{-}2ClO_4]^{2+}$), 561.7104 ($[D1\text{-}3ClO_4]^{3+}$), 396.55 ($[D1\text{-}4ClO_4]^{4+}$).

$[Ru_2(dmbpy)_4(PyiP\text{-}methane)](ClO_4)_4$(D2). Yield: 61%. IR (KBr): $\tilde{\nu} =$ 3071 (C-H aromatic), 2959 (C-H aliphatic), 1617 (C=C), 1609 (C=N), 1541, 1088 (ClO_4) cm^{-1}. ^{1}HNMR (250 MHz, D_6-DMSO): 9.05 (d, J = 10 Hz, 2H), 8.78-8.51 (m, 12H), 8.11 (d, J = 7.5 Hz, 2H), 8.05-7.88 (m, 6H), 7.85-7.56 (m, 10H), 7.63-7.33 (m, 12H), 7.31-7.11 (m, 8H), 4.39 (s, 2H, Hydrogens of -CH_2- as alkyl spacer), (24H, Signal of hydrogens of methyl groups on dmbpy are buried under DMSO peak). ^{13}CNMR (62 MHz, D_6-DMSO): 156.62, 151.73, 150.93, 150.40, 150.06, 149.85, 148.29, 146.26, 146.00, 144.40, 136.99, 136.67, 134.77, 131.56, 130.60, 129.43, 128.93, 128.45, 128.04, 127.41, 126.13, 125.84, 125.48, 124.90, 123.87, 123.12, 121.75, 21.13 (carbon of methyl group of dmbpy), (^{13}C Signal of -CH_2- as alkyl spacer is buried under D_6-DMSO peak at 39-41 ppm). Anal. calcd. For $C_{97}H_{78}Cl_4N_{18}O_{16}Ru_2$ (%): C, 55.59; H, 3.75; N, 12.03. Found (%): C, 55.58; H, 3.76; N, 12.13. TOF-MS (CH_3OH, m/z): 948.62 ($[D2\text{-}2ClO_4]^{2+}$), 598.75 ($[D2\text{-}3ClO_4]^{3+}$), 424.58 ($[D2\text{-}4ClO_4]^{4+}$).

Synthesis of $[Ru_2(dmbpy)_4(PyiP\text{-}methane\ (CH_3)_2)](ClO_4)_6$ (D3): 0.1 mmol of D2 in 8 ml acetonitrile was degassed by nitrogen for 5 min. Then, 0.5 mmol of methyl iodide was added to the solution and heated under N_2 at 40 °C for 14 h. After, the solvent was removed under reduced pressure, the residue was dissolved in 5 ml methanol and precipitated by dropwise addition of saturated $NaClO_4$ solution. The product was collected by centrifuge and several time washed with deionized water and purified by column chromatography on alumina with acetonitril-toluene (3/1, v/v) as an eluent. Yield: 62%. Anal. calcd. For $C_{99}H_{84}Cl_6N_{18}O_{24}Ru_2$ (%): C, 51.15; H, 3.64; N, 10.85, Found (%): C, 51.11; H, 3.65; N, 10.83. ^{1}HNMR (250 MHz, D_6-DMSO): 9.46 (d, J = 15 Hz, 2H), 9.12 (d, J = 7.5 Hz, 2H), 8.95 (m, 4H) 8.70 (m, 6H), 8.34-8.13 (m, 4H), 8.11-7.95 (m, 6H), 7.92-7.77 (m, 6H), 7.77-7.46 (m, 12H), 7.46-7.26 (m, 6H), 7.17 (d, J = 7.5 Hz, 4H), 4.44 (s, 6H, Hydrogens of methyl pridinium moeity of PyIP), 4.39 (s, 2H, Hydrogens of -CH_2- as alkyl spacer), (24H, Signal of hydrogens of methyl groups on dmbpy are buried under DMSO peak). ^{13}CNMR (62 MHz, D_6-DMSO): 156.59, 150.97, 150.15, 147.64, 146.78, 146.44, 145.94, 144.44, 143.43, 136.70, 134.62,133.80, 132.02, 130.43, 129.35, 129.04, 128.46, 127.69, 126.35, 125.73, 125.50, 122.26, 121.78, 49.01 (carbon of methyl of pyridinium moeity), 21.14 (carbon of methyl group of dmbpy), (^{13}C Signal of -CH_2- as alkyl spacer is buried under D_6-DMSO peak at 39-41 ppm). TOF-MS (CH_3OH, m/z): 1062.12 ($[D3\text{-}2ClO_4]^{2+}$), 675.74 ($[D3\text{-}3ClO_4]^{3+}$), 481.57 ($[D3\text{-}4ClO_4]^{4+}$).



Scheme S1. Synthesis of phenanthroimidazole ligand (PyiP-methane) and their derivative dinuclear ruthenium(II) complexes

3. NMR specrta

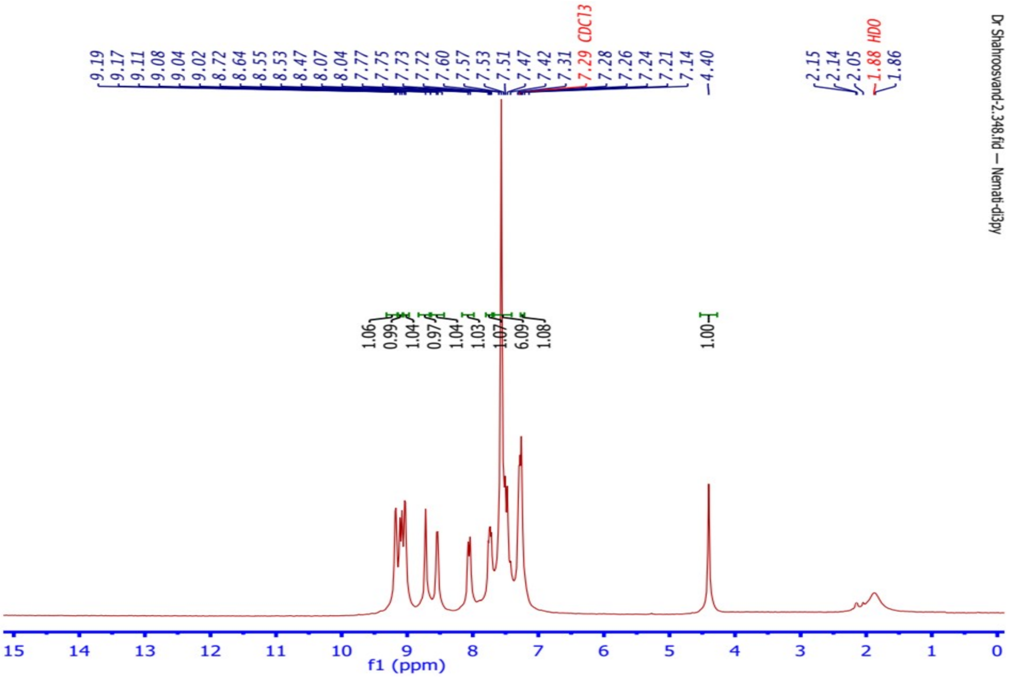


Figure S1. ^{1}HNMR of PyiP -methane in CDCl$_3$

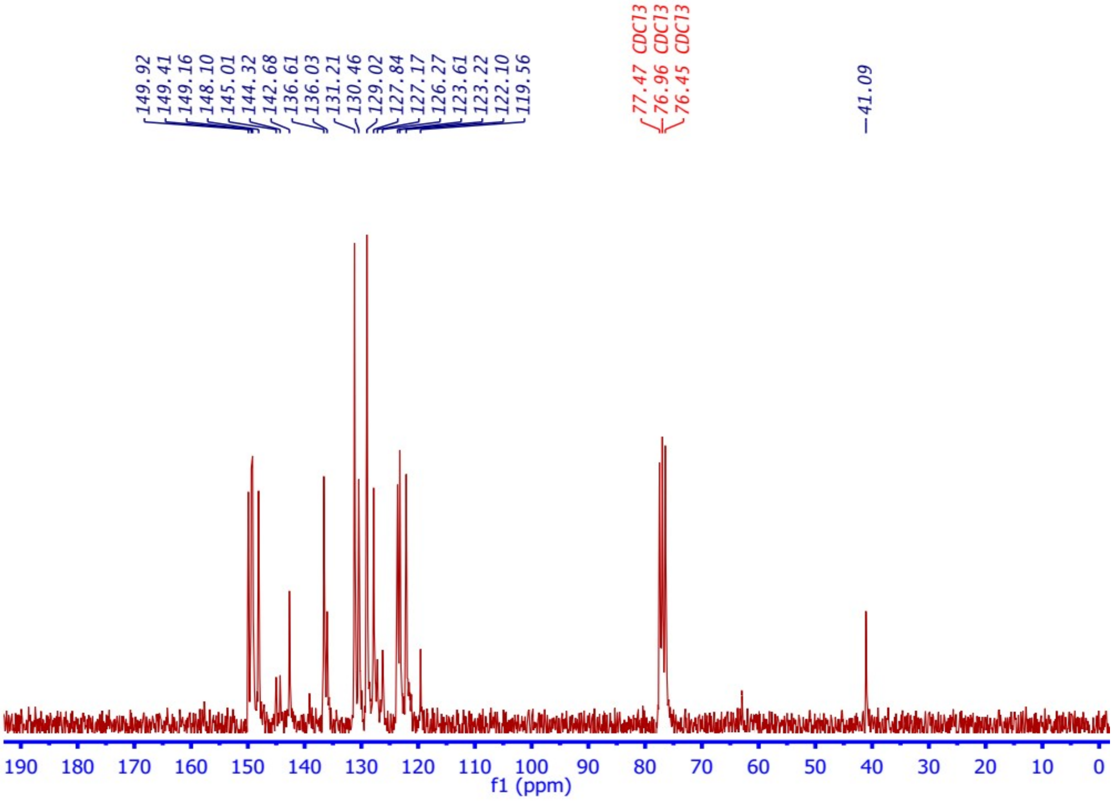


Figure S2. ^{13}CNMR of PyiP-methane in $CDCl_3$

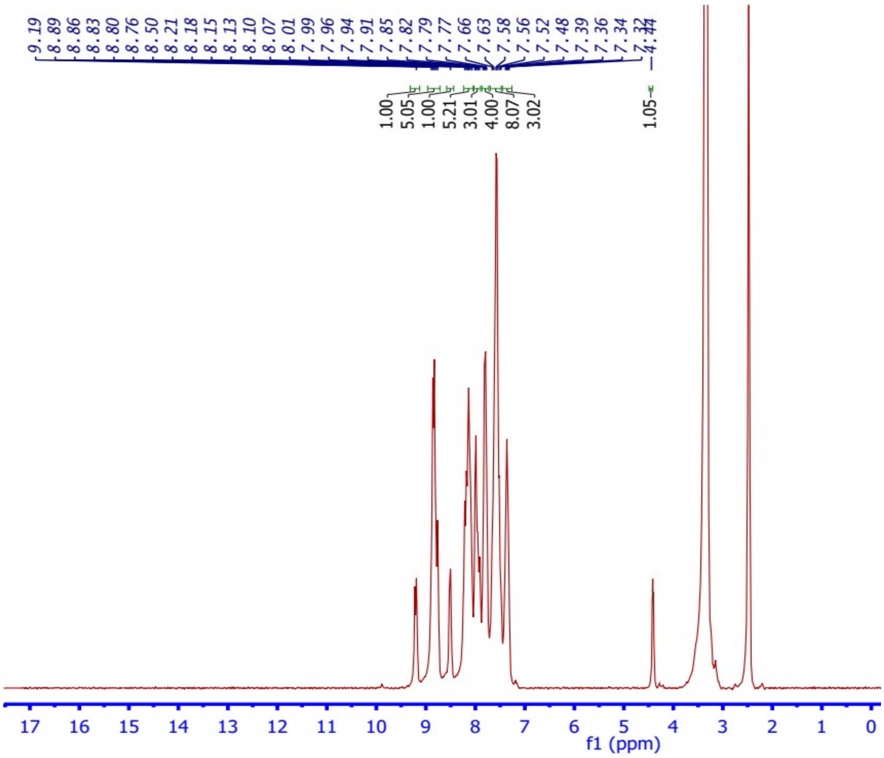


Figure S3. ^{1}HNMR of D1 in D_6-DMSO

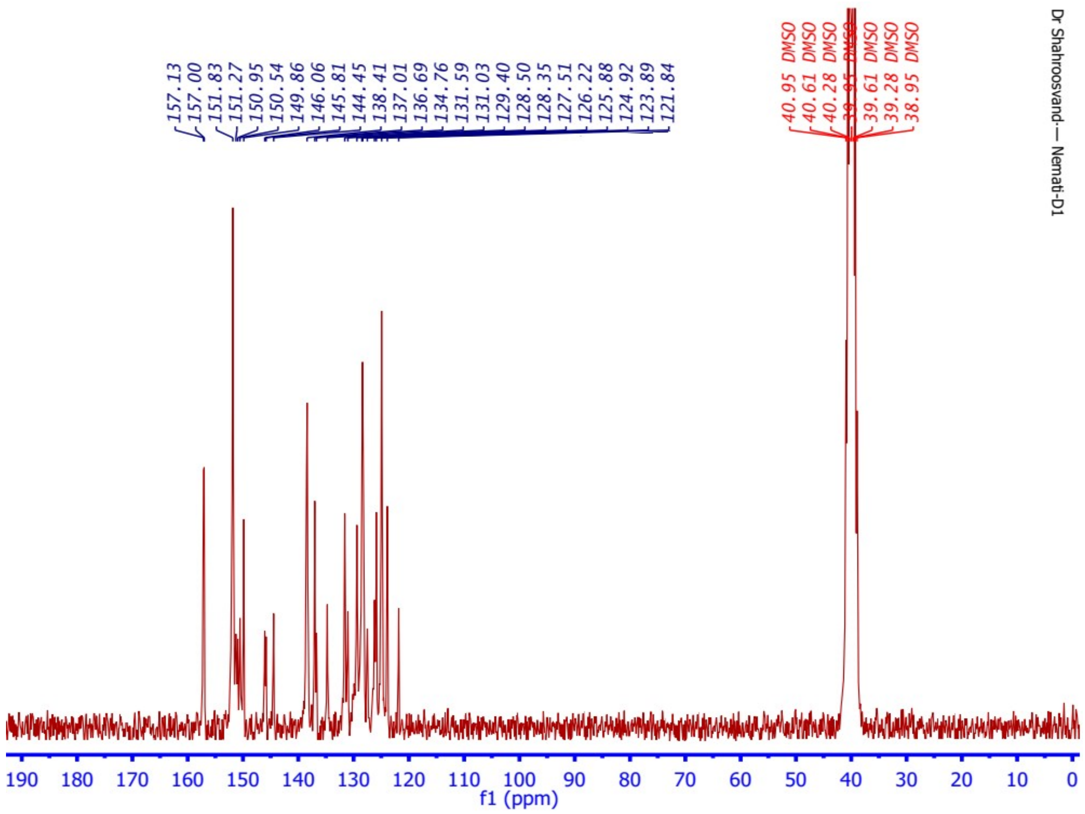


Figure S4. ^{13}CNMR of D1 in D_6-DMSO

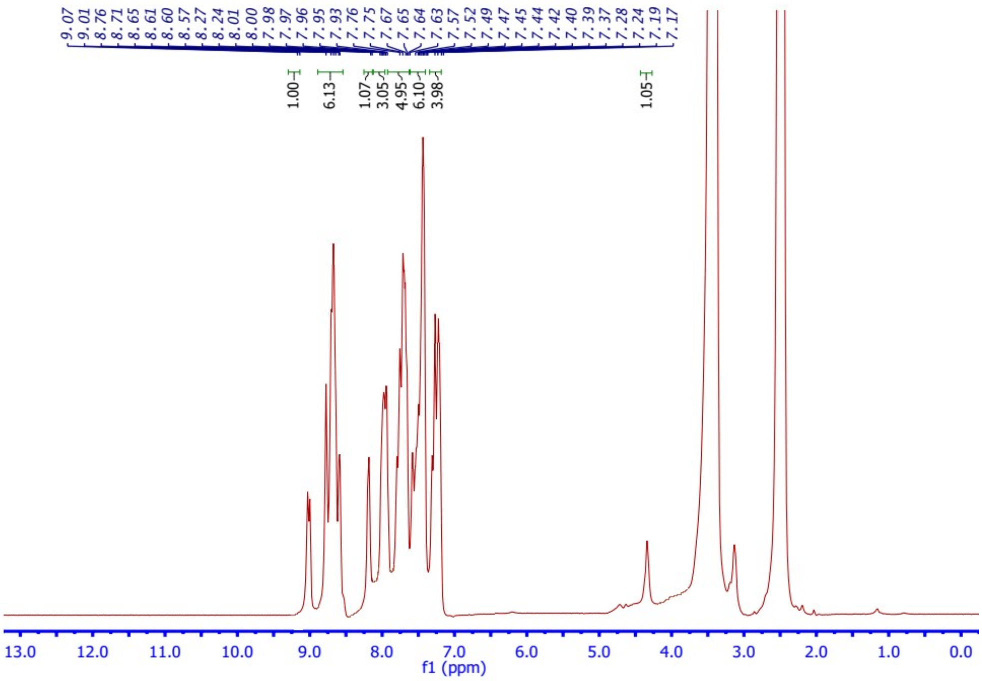


Figure S5. ^{1}HNMR of D2 in D_6-DMSO

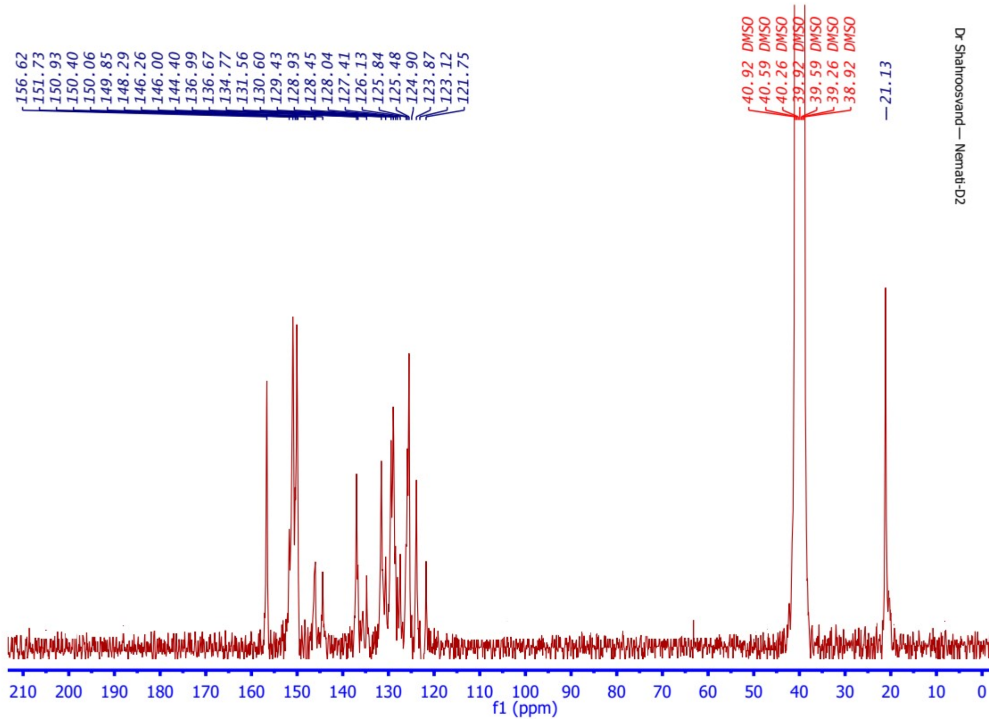


Figure S6. ^{13}CNMR of D2 in D_6-DMSO

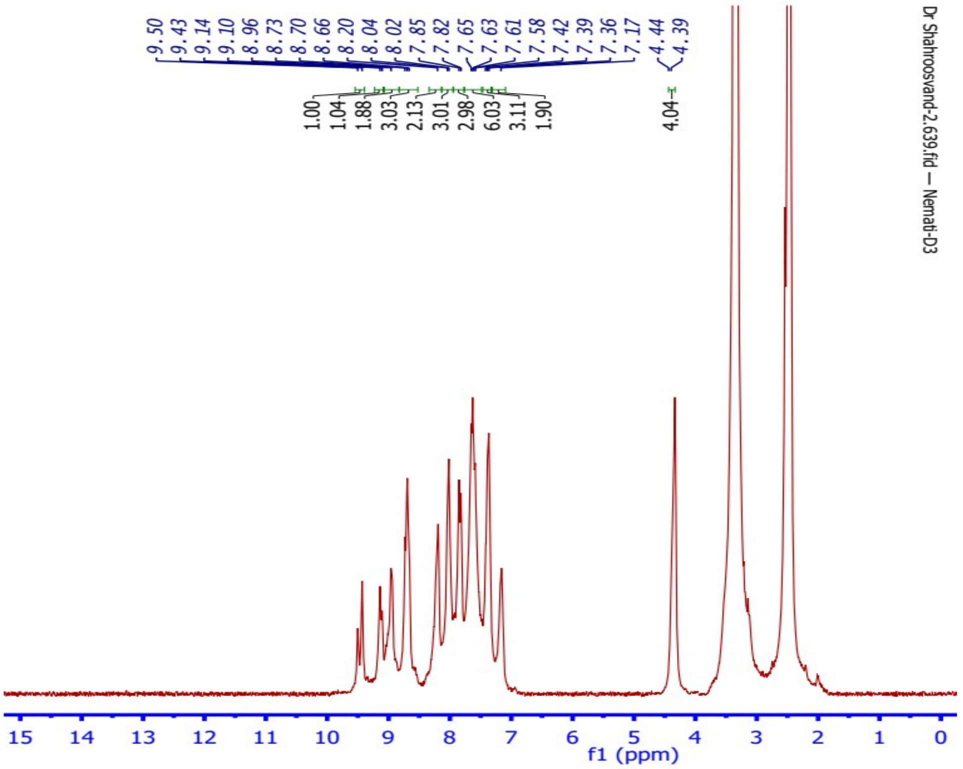


Figure S7. ^{1}HNMR of D3 in D_6-DMSO

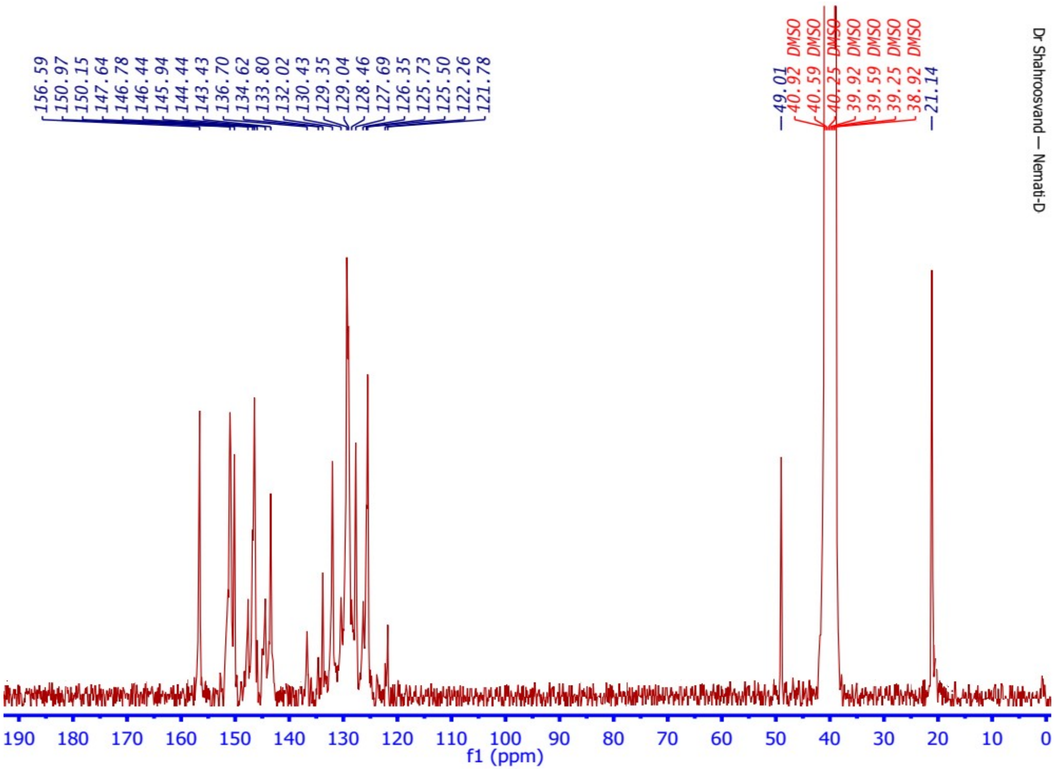


Figure S8. ^{13}CNMR of D3 in D_6-DMSO

4. Mass spectra

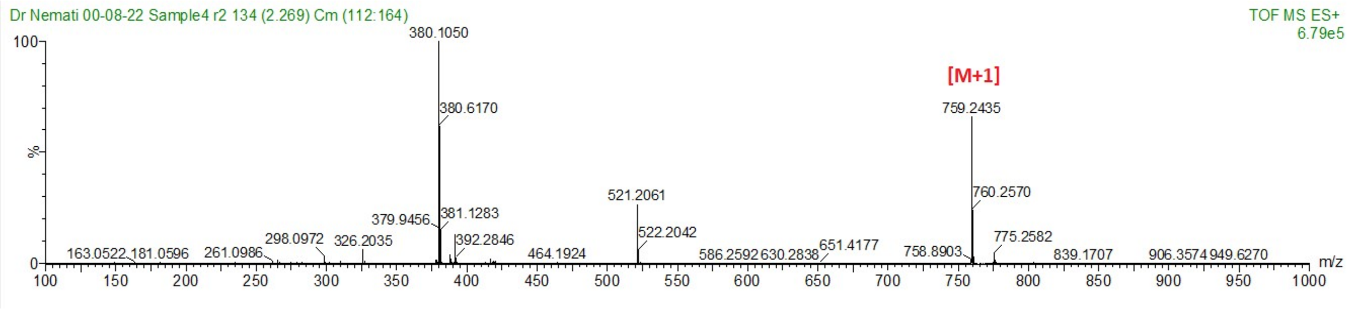


Figure S9. TOF-MS spectrum of bridging ligand

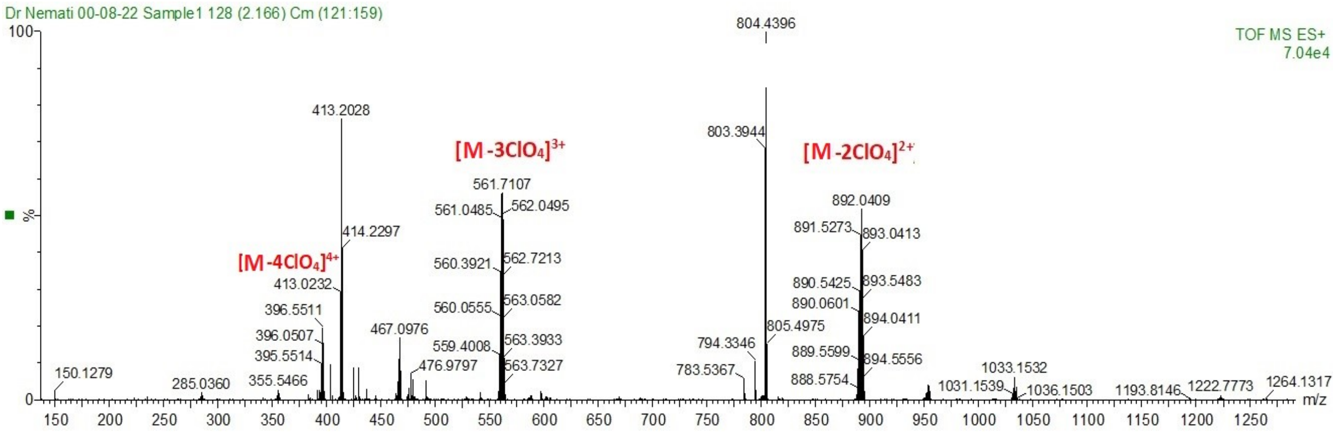


Figure S10. TOF-MS spectrum of D1

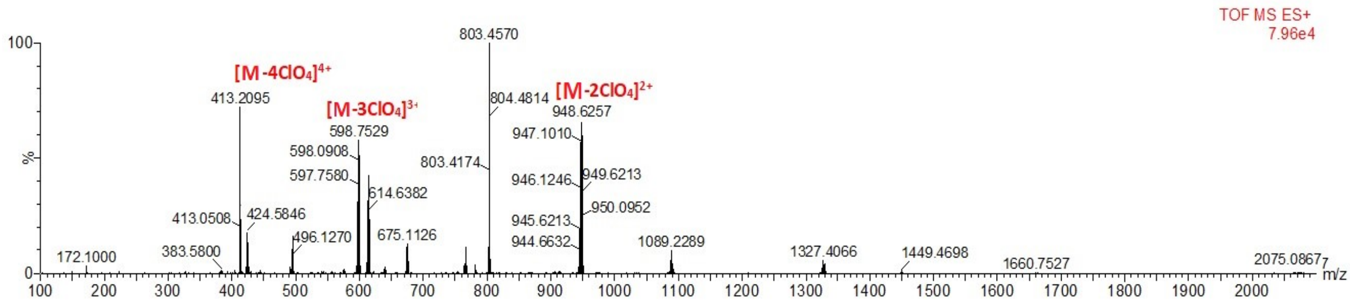


Figure S11. TOF-MS spectrum of D2

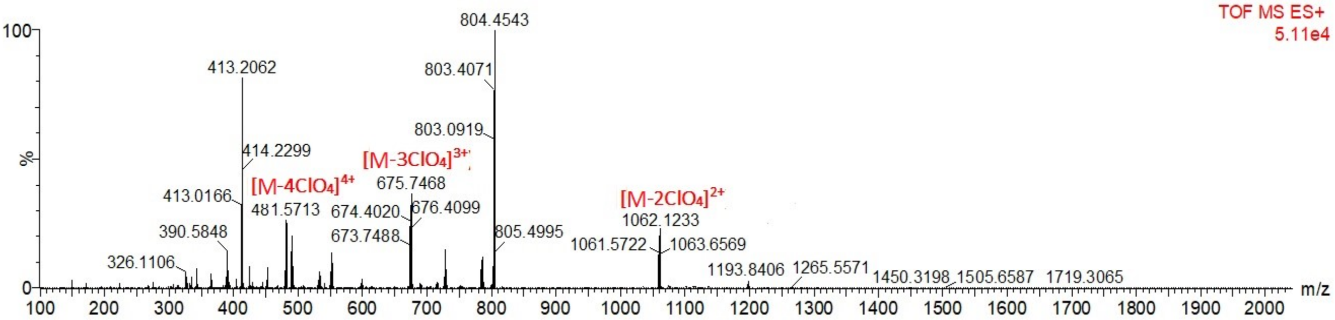


Figure S12. TOF-MS spectrum of D3

5. Photophysical

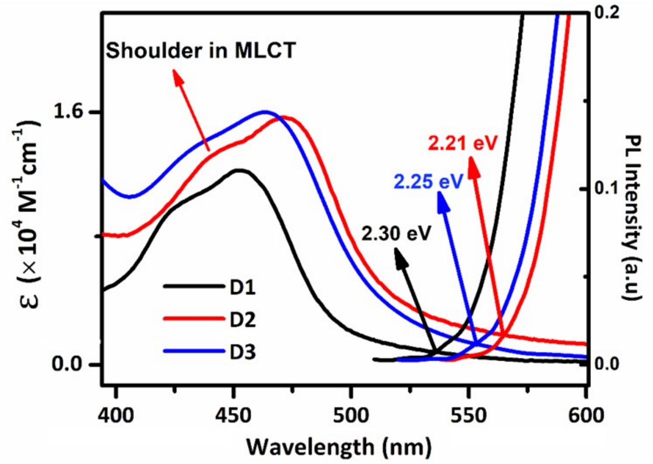


Figure S13. Zoomed MLCT region in the UV-Vis /emission spectra (400-600 nm) to show the intersection of absorption and emission spectra (E_{0-0})

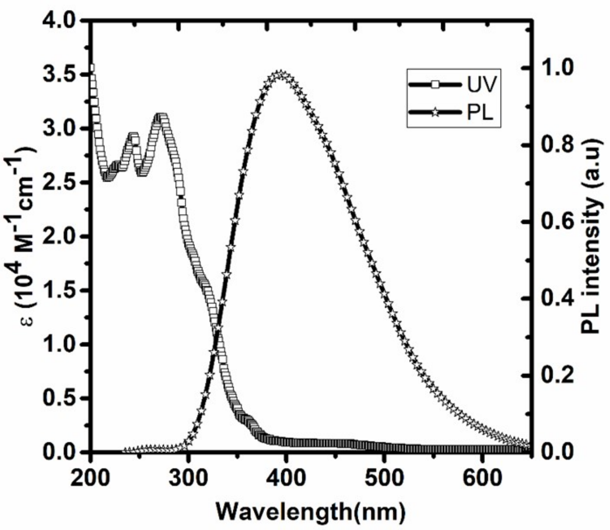


Figure S14. UV-Vis /emission (λ_{exc}=280 nm) spectra of bridging ligand in the acetonitrile solution.

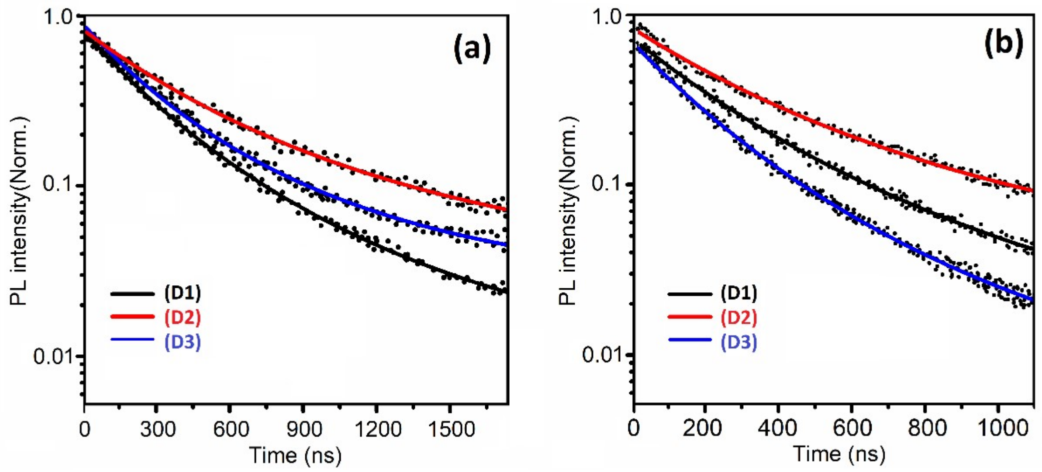


Figure S15. Excited-state lifetimes of degassed acetonitrile solution (a) and thin film (b) of complexes

6. Electrochemical

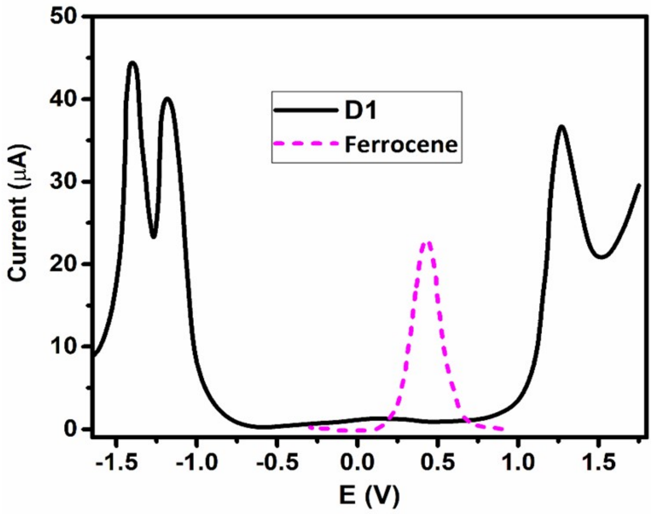


Figure S16. Comparision of DPV of binuclear (D1) and mononuclear (equimolar solution, 10^{-5} M) complex.

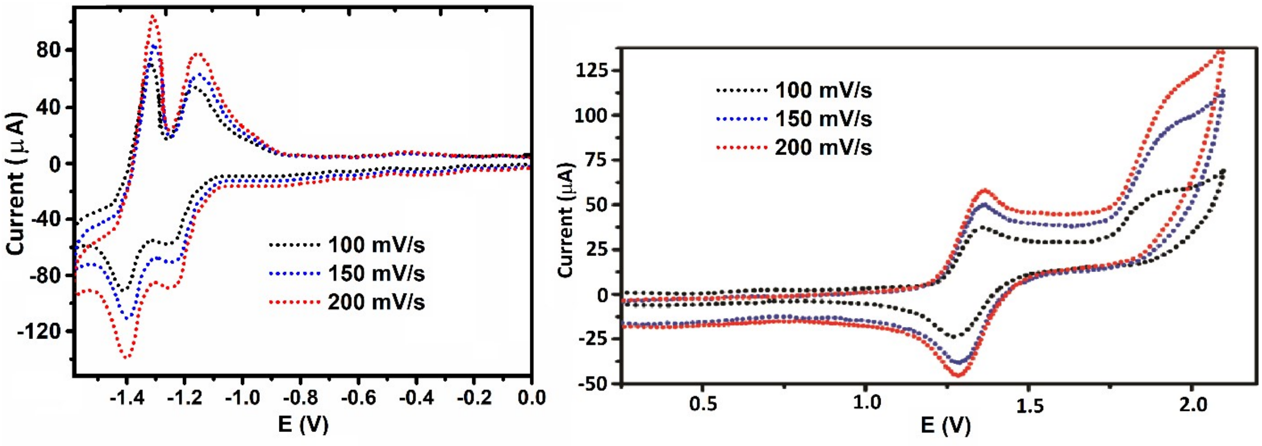


Figure S17. Cyclic voltamogram of D1 at different scan rate. Negative window (left), positive window (right)

7. SEM figures

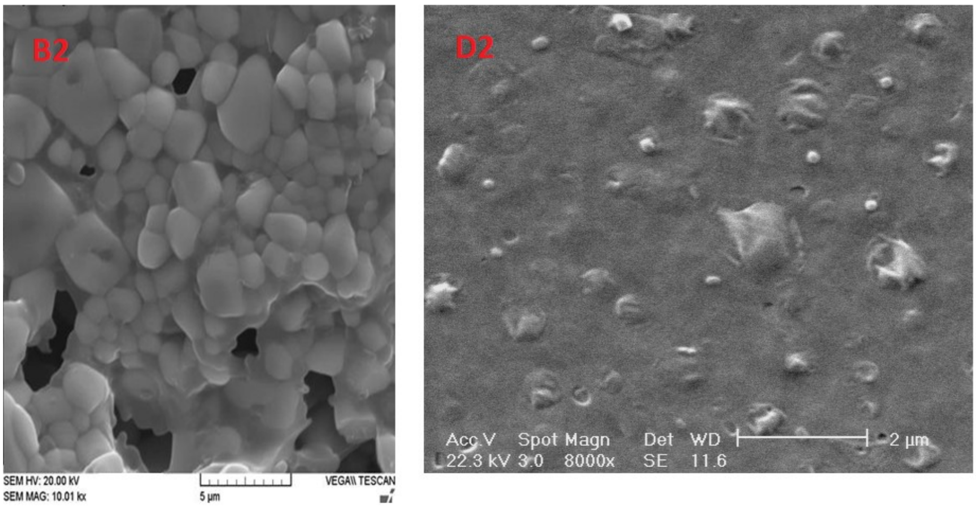


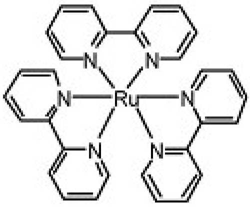
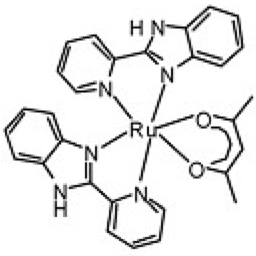
Figure S18. Top view SEM images of surfaces of ITO coated with B2 (previous work, ref. 12) and D2 (This work) complexes.

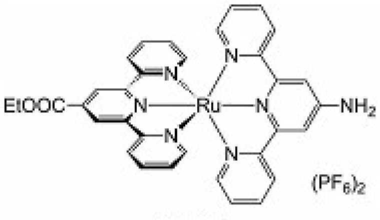
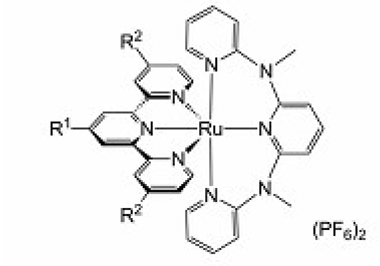
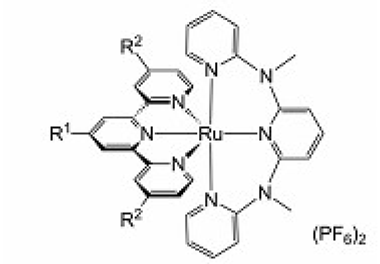
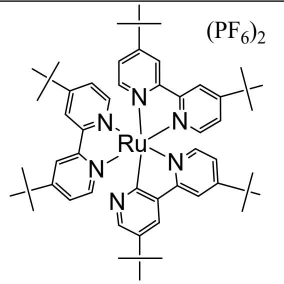
8. Tables

Table S1. The main data of time resolved photoluminescence decay for D1-D3 complexes in acetonitrile solution and neat-film.

Complex	D1 in ACN (615nm)	D1 as Film (626 nm)	D2 in ACN (637 nm)	D2 as Film (683 nm)	D3 in ACN (629 nm)	D3 as Film (675 nm)
X^2	0.997	0.998	0.999	0.993	0.996	0.997
A_1	0.11	0.58	0.23	0.64	0.19	0.66
τ_1(ns)	29	169	46	249	39	152
A_2	0.89	0.42	0.77	0.36	0.81	0.34
τ_2 (ns)	292	304	483	484	389	249
τ_{av} (ns)	293	245	472	371	380	197

Table S2. EL properties of near infrared light electrochemical cell based on **mononuclear ruthenium** polypyridyl complexes

Mononuclear ruthenium complexes	Cell configuration	EL_{max} (nm)	EQE(%)	Ref.
	ITO/complex(90)/ Ga:In	660	1.4	(4)
	ITO/complex (100 nm)/Au (100 nm)	630	0.31	(5)
	ITO/complex (100 nm)/Au (100 nm)	880	0.075	(5)

	ITO/complex (100 nm)/Au (100 nm)	900	0.06	(5)
	ITO/complex (100 nm)/Au (100 nm)	945	0.03	(5)
 [1](PF$_6$)$_2$	ITO/PEDOT:PSS(45nm)/Ru:PMMA (169-194 nm)/Ag	733	0.001	(6)
 [2](PF$_6$)$_2$: R^1 = COOEt; R^2 = H	ITO/PEDOT:PSS(45nm)/Ru:PMMA (169-194 nm)/Ag	722	0.028	(6)
 [3](PF$_6$)$_2$: R^1 = R^2 = COOMe	ITO/PEDOT:PSS(45nm)/Ru:PMMA (169-194 nm)/Ag	745	0.013	(6)
	ITO/PEDOT:PSS(30nm)/Ru/A	600, 720	2.06 ,0.27(after 100 min)	(7)

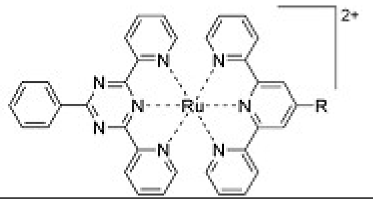
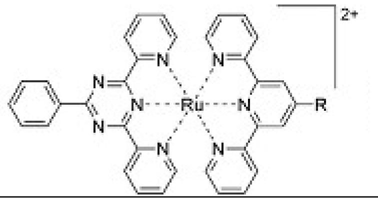
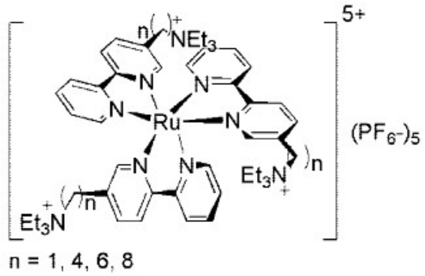
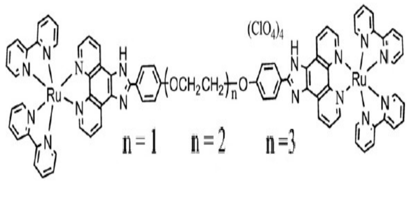
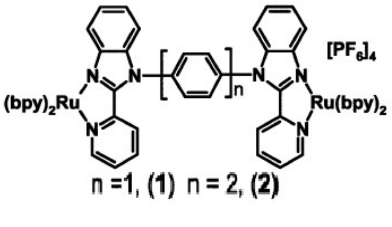
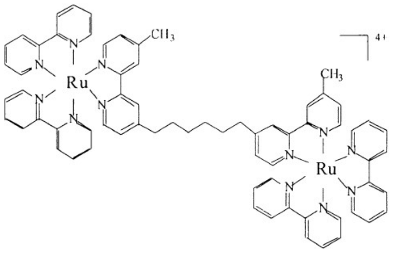
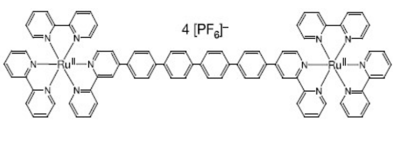
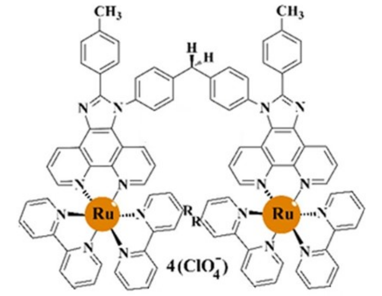
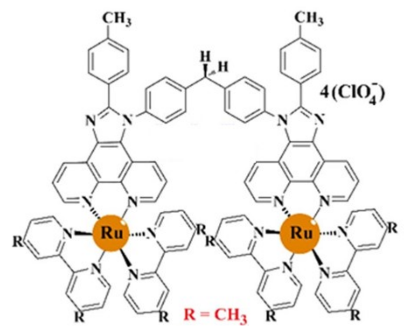
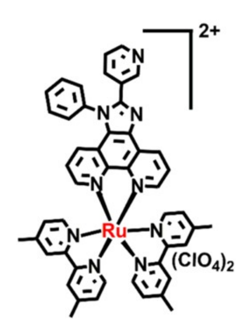
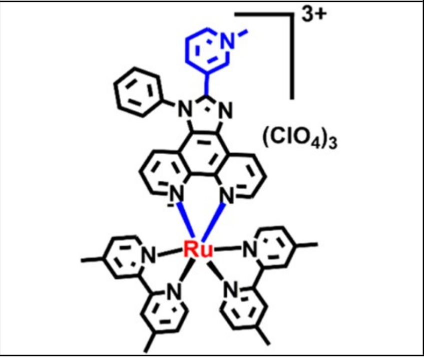
 **1**: R=H	TO/PEDOT:PSS/complex:PMMA/Al	717	0.005	(8)
 **2**: R= CO_2Et	TO/PEDOT:PSS/complex:PMMA/Al	725	0.005	(8)
	ITO/[Ru complex]/Au	n=1, 612 n=4, 599 n=6, 599 n=8, 605	n=1, 0.01 n=4, 0.17 n=6, 0.43 n=8, 0.27	(9)

Table S3 EL properties of light emitting electrochemical cell based on **dinuclear ruthenium** polypyridyl complexes

Dinuclear ruthenium complexes	**Cell configuration**	EL_{max} (nm)	V_{on} (V)	L_{max} (cd.m^{-2}) (at voltage)	EQE(%)	Device Lifetime	**Ref.**
	ITO/complex (100 nm)/Au (100 nm)	780	-	-	0.013	-	(5)

	ITO/complex (100 nm)/Au (100 nm)	1040	-	-	-	-	(5)
	ITO/complex(90)/Ga:In	n=1, 638 n=2, 626 n=3, 611	n=1, 2.3 n=2, 2.4 n=3, 2.4	n=1, 310 (5.8V) n=2, 365 (5.8)V n=3, 310 (5.5) V	-	-	(10a)
	ITO/complex /Al(100 nm)	n=1, 637 n=2, 657	n=1, 3.2 n=2, 3.5	n=1, 86 (at 5V) n=2, 133 (at 7V)	-	-	(1)
	ITO/ Ru/ Li-triflate /Cr	638	6.8	-	0.02 (at 4V)	-	(10b)
	ITO/Ru:PPV (1:5) /Al(100 nm)	≈630 (at 4V) ≈530 (at -4V)	-	25 (at 4V) 330 (at -4V)	-	-	(10c)

	ITO/complexes (90nm)/ Ga:In	635	4.5	193 (at 7.4)	0.141 (at 7.5 V)	9 min	11
		690	3.1	742 (at 7.7)	0.682 (at 5.9 V)	18 min	11
	ITO/complexes (90nm)/ Ga:In	695	2.6	2229	0.62	94 min	12
		706	2.3	1248	0.16	8.2 min	12

References:

1. W.-L. Jia, Y.-F. Hu, J. Gao and S. Wang, *Dalton Transactions*, 2006, 1721-1728.

2. K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Physical Chemistry Chemical Physics*, 2009, **11**, 9850-9860.

3. (a) B. Sullivan, D. Salmon and T. Meyer, *Inorganic chemistry*, 1978, **17**, 3334-3341. (b) J. Collin and J. P. Sauvage, *Inorganic Chemistry*, 1986, **25**, 135-141.(c) R. Caspar, C. Cordier, J. B. Waern, C. Guyard-Duhayon, M. Gruselle, P. Le Floch and H. Amouri, *Inorganic chemistry*, 2006, **45**, 4071-4078.(d) W. Paw and R. Eisenberg, *Inorganic chemistry*, 1997, **36**, 2287-2293.

4. F. G. Gao and A. J. Bard, *Chemistry of materials*, 2002, **14**, 3465-3470.

5. S. Xun, J. Zhang, X. Li, D. Ma and Z. Y. Wang, *Synthetic metals*, 2008, **158**, 484-488.

6. A. Breivogel, M. Park, D. Lee, S. Klassen, A. Kühnle, C. Lee, K. Char and K. Heinze, *European Journal of Inorganic Chemistry*, 2014, **2014**, 288-295.

7. J.-H. Hsu and H.-C. Su, *Physical Chemistry Chemical Physics*, 2016, **18**, 5034-5039.

8. H. J. Bolink, E. Coronado, R. n. D. Costa, P. Gaviña, E. Ortí and S. Tatay, *Inorganic chemistry*, 2009, **48**, 3907-3909.

9. E. Zysman-Colman, J. D. Slinker, J. B. Parker, G. G. Malliaras and S. Bernhard, *Chemistry of materials*, 2008, **20**, 388-396.

10. (a) C.-C. Ju, C.-H. Chen, C.-L. Yuan and K.-Z. Wang, *Thin solid films*, 2011, **519**, 3883-3889.(b) J.-C. Leprêtre, A. Deronzier and O. Stéphan, *Synthetic metals*, 2002, **131**, 175-183.(c) S. Welter, K. Brunner, J. Hofstraat and L. De Cola, *Nature*, 2003, **421**, 54-57.

11. B. N. Bideh and H. Shahroosvand, *Scientific reports*, 2017, **7**, 1-7.

12. B. Nemati Bideh, H. Shahroosvand and M. K. Nazeeruddin, *Inorganic Chemistry*, 2021, **60**, 11915-11922.