

Supplementary information

Going from green to red color electroluminescence through ancillary ligand substitution in ruthenium(II) tetrazole benzoic acid emitters

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S1:

The wavelength of electroluminescence (EL) and photoluminescence (PL) emissions of reported ruthenium complexes.

Complex/reactant	λ_{em} (nm)	λ_{EL} (nm)	ref
$Ru(bpy)_3^{2+}$	608	608	1,2,3
$Ru(bpy)_3^{2+}/C_2O_4^{2-}$	610	610	4
$Ru(bpy)_3^{2+}/C_2O_4^{2-}$		591	5
$Ru(bpy)_3^{2+}/S_2O_8^{2-}$	625	625	4,6
$Ru(bpy)_3^{2+}/TPrA$	610	610	7
$Ru(dmbp)_3^{2+}/C_2O_4^{2-}$		594	5
$Ru(phen)_3^{2+}$	590	590	8
$Ru(phen)_3^{2+}/C_2O_4^{2-}$		585	5
$Ru(dmphen)_3^{2+}/C_2O_4^{2-}$		591	5
$Ru(terpy)_3^{2+}$		660	8
$Ru(bpz)_3^{2+}$	585	585	9,10
$Ru(bpz)_3^{2+}/S_2O_8^{2-}$	585	590	11
$Ru(dp-bpy)_3^{2+}$	635	635	12

$\text{Ru}(\text{dp-phen})_3^{2+}$	615	615	12
$(\text{bpy})_2\text{Ru}(\text{bphb})^{2+}$	624	624	13
$(\text{bpy})_2\text{Ru}(\text{bphb})^{2+} / \text{TPrA}$	624	624	13
$(\text{bpy})_2\text{Ru}(\text{bphb})^{2+} / \text{S}_2 \text{O}_8^{2-}$	624	624	13
$[(\text{bpy})_2\text{Ru}]_2(\text{bphb})^{4+}$	624	624	13
$[(\text{bpy})_2\text{Ru}]_2(\text{bphb})^{4+} / \text{TPrA}$	624	624	13
$[(\text{bpy})_2\text{Ru}]_2(\text{bphb})^{4+} / \text{S}_2 \text{O}_8^{2-}$	624	624	13
$(\text{bpy})_2\text{Ru}(\text{AZA-bpy})^{2+} / \text{TPrA}$	603	603	14
$(\text{bpy})_2\text{Ru}(\text{AZA-bpy})^{2+} / \text{TPrA}$	613	613	14
$(\text{bpy})_2\text{Ru}(\text{CE-bpy})^{2+} / \text{TPrA}$		650	15
$(\text{bpy})_2\text{Ru}(\text{CE-bpy})^{2+} / \text{TPrA}$		655	15
$\text{Ru}(\text{v-bpy})_3^{2+}$	630	650	16
$(\text{bpy})_2\text{Ru}(\text{DC-bpy})^{2+}$	629	629	17
$(\text{bpy})_2\text{Ru}(\text{DM-bpy})^{2+}$	605	605	17
$(\text{bpy})_2\text{Ru}(\text{dpen-bpy})^{2+} / \text{PF}_6^-$	612	612	18

$\text{Ru(m-bpy)}_3^{2+} / \text{PF}_6^-$	609	612	18
$\text{Ru(dtb-bpy)}_3^{2+} / \text{PF}_6^-$	610	611	18
$(\text{bpy})_2\text{Ru(DIM)}^{2+}$	600	600	19
$(\text{bpy})_2\text{Ru(PBIm-H)}^{2+} / \text{PF}_6^-$		680	20
$[\text{Ru(tpy)(tpy-COOEt)}] / \text{PF}_6^-$	706	706	21
Ru(DM-bpy)_3^{2+}	604	615	22
$(\text{bpy})_2\text{Ru(dbeb)}^{2+} / \text{PF}_6^-$	642	640	23
$(\text{bpy})_2\text{Ru(pbq)}^{2+}$	900	900	24
$(\text{PBIm-H})_2\text{Ru(pbq)}^{2+}$	945	945	24
$(\text{PBIm-H})_2\text{Ru(acac)}^{2+}$	850	880	24
$[\text{Ru(PBIM-H)}_2]_2(\text{pbq})^{+2}$	1040	1040	24
$\text{Ru(tpy)(trz)}^{2+} / \text{PF}_6^-$	723	717	25
$\text{Ru(tpy-COOEt)(trz)}^{2+} / \text{PF}_6^-$	717	725	25
$(\text{bpy})_2\text{Ru(Mt-bpy)}^{2+} / \text{PF}_6^-$	625	557	26

RuTRu	625	598	26
(bpy) ₂ Ru(aa-bpy) ²⁺ /PF ₆ ⁻	649	699	27
Ru ₂ (bpy) ₄ (im-phen) / ClO ₄ ⁻	638	655	28
(bpy) ₂ Ru(Eh-bpy) ²⁺ /PF ₆ ⁻	427	600	29
(bpy) ₂ Ru(Hmh-bpy) ²⁺ /PF ₆ ⁻	427	600	29
(H ₂ MPy ₃ ,4DMPP)Ru(bpy) ₂ Cl /PF ₆ ⁻	655	656	30
Ru ₂ (bpy) ₂ (tpy) ₂ (BTB) ²⁺	680	710	31
Ru ₂ (bpy) ₂ (tpy) ₂ (4-TBN) ³⁺	676	680	31
[Ru(bpy) ₂] ₂ (bmpa-bpy) ⁺² /PF ₆ ⁻	642	596	32
[Ru(bpy) ₂] ₂ (bmdpa-bpy) ⁺² /PF ₆ ⁻	638	570	32
[Ru(bpy) ₂] ₂ (bmna-bpy) ⁺² /PF ₆ ⁻	636	570	32

m-bpy = 4-methyl-2,2'-bipyridine

dtb-bpy = 4,4'-di-tert-butyl-2,2'-bipyridine

dpen-bpy = 4,4'-di-n-pentyl-2,2'-bipyridine

DIM = 4,7-dimethyl-1,10-phenanthroline

PBI-m-H = 2-(2-pyridyl)-1H-benzimidazole

tpy = 2,2',6',2''-terpyridine

tpy-COOEt = 2,2',6',2'', terpyridine-4'-carboxylic acid ethyl ester

DM-bpy = 4,4'-dimethyl-2,2'- bipyridine

dbeb = 4,4'-dibutyl ester-2,2'-bipyridine

pbq = 2,3-bis(2-pyridyl)benzoquinoline

acac = acetylacetonate

trz = 2-phenyl-4,6-dipyridin-2-yl-1,3,5-triazine

RuTRu = bis-2,2'-bipyridyl-ruthenium-bis-[2-((E)-4'-methyl-2,2'-bipyridinyl-4)-ethenyl]-thienyl-bis-2,2'-bipyridyl-ruthenium tetra hexafluorophosphate

Mt-bpy = 4-methyl-4'-(2-thienylethenyl)-2,2'-bipyridine

aa-bpy = Acrylic acid 4'-acryloyloxymethyl-2,2'-bipyridinyl-4-ylmethyl ester

im-phen = 1,2-bis(4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenoxy)ethane

Eh-bpy = 4,4'-bis(3-ethylheptyl)-2,2'-bipyridine

Hmh-bpy = 4-dihexylmethyl-4'-heptyl-2,2'-bipyridine

H2MPy3,4DMPP = meso-tris-3,4-dimethoxyphenyl-mono-(4-pyridyl)porphyrin

4-TBN = 4-(1H-tetrazol-5-yl)benzotrile

BTB = bis(1H-tetrazol-5-yl)benzene

bpy = 2,2'-bipyridine

C₂ O₄²⁻ = oxalate ion

S₂ O₈²⁻ = persulfate or peroxydisulfate

TPrA = tri-n-propylamine

dmbp = 4,4'-Me₂bpy and **DM-bpy** = 4,4'-dimethyl-2,2'-bipyridine

phen = 1,10-phenanthroline

terpy = 2,2',2''-terpyridine

bpz = 2,2'-bipyrazine

dp-bpy = 4,4'-biphenyl-2,2'-bipyridyl

dp-phen = 4,7-diphenyl-1,10-phenanthroline

dmphen = 4,7-dimethyl-1,10-phenanthroline

bphb = 1,4-bis(4'-methyl-2,2'-bipyridin-4-yl)benzene

AZA-bpy = 4-(N-aza-18-crown-6-methyl-2,2'-bipyridine

CE-bpy= bipyridine ligand where a crown ether (15-crown 5) is bound to the bpy ligand in the 3- and 3'-positions

v-bpy =4-vinyl-4'-methyl-2,2'-bipyridine

DC-bpy = 4,4'-dicarboxy-2,2'-bipyridine

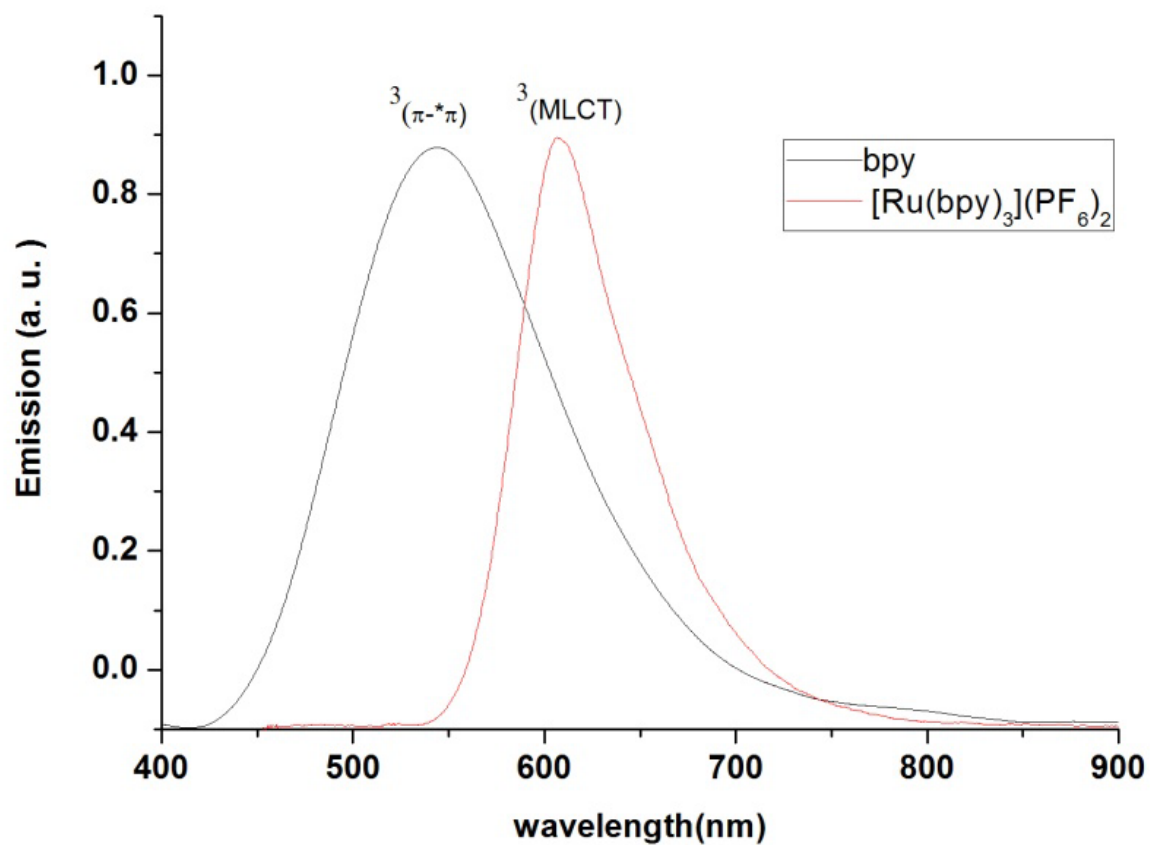
PF₆⁻ =hexafluorophosphate

bmpa-bpy =bis(4'-methyl-2,2'-bipyridinyl-4-carbonyl)-(1,4-phenylenediamine)

bmdpa-bpy =bis(4'-methyl-2,2'-bipyridinyl-4-carbonyl)-(1,4-diphenylenediamine)

bmna-bpy =bis(4'-methyl-2,2'-bipyridinyl-4-carbonyl)-(1,4-naphthalenediamine)

S2: PL emission spectra of bpy ligand and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in DMF solution $10^{-5} \text{ mol lit}^{-1}$ ($\lambda_{\text{exc}}=405 \text{ nm}$).



S3 : Photophysical properties of ruthenium tetrazole derivatives .

Ruthenium tetrazole derivatives	PL		EL		ref
	Φ	τ	$\lambda_{(max)}$	rECL-Int. (%)	
[Ru(2-TT)(tpy)(bpy)] ⁺	<0.001	18.64	-	-	[33]
[Ru{2-(Me)TT} (tpy)(bpy)] ²⁺	<0.001	22.10	-	-	[33]
[Ru{2-(H)TT} (tpy)(bpy)] ²⁺	<0.001	18.44	-	-	[33]
[Ru(2-TBT) (tpy)(bpy)] ⁺	<0.001	15.79	-	-	[33]
[Ru(Me)(2-TBT) (tpy)(bpy)] ²⁺	<0.001	-	-	-	[33]
[(tpy)(bpy)Ru(TDT)Ru(tpy)(bpy)] ²⁺	<0.001	19.34	-	-	[33]
[(tpy)(bpy)Ru(Me)(TDT)(Me)Ru(tpy)(bpy)] ⁴⁺	<0.001	22.15	-	-	[33]
[Ru(4-(Me)TBN)(tpy)(bpy)] ²⁺	0.008	-	-	-	[34]
[Ru(4-TBN)(tpy)(bpy)] ⁺	0.003	-	-	-	[34]
[(tpy)(bpy)Ru(BTB)Ru(tpy)(bpy)] ²⁺	0.003	-	710	45	[34]
[(tpy)(bpy)Ru(4-TBN)Ru(tpy)(bpy)] ²⁺	0.008	-	680	120	[34]
[Ru(bpy) ₂ (pyTz)] ²⁺	0.004 ^a	220	-	-	[35]
[Ru(bpy) ₂ (pyrTz)] ²⁺	0.003 ^a	6	-	-	[35]
[Ru(bpy) ₂ {4-Me-(pyTz)}] ²⁺	0.001 ^a	160(10)	-	-	[35]
[Ru(bpy) ₂ {4-Me(pyrTz)}] ²⁺	0.003	150	-	-	[35]
[Ru(bpy)(tpy)(TPh)] ⁺	0.003	-	740	75	[36]
[Ru(bpy)(tpy)(4-pyTz)] ⁺	0.004	-	730	15	[36]
[Ru(bpy)(tpy)(4-Me(TBN)] ⁺	0.006	-	720	45	[36]
[(tpy)(bpy)Ru(BTB)Ru(bpy)(tpy)] ²⁺	0.005	-	700	45	[36]
[Ru(bpy) ₃] ²⁺	0.06	-	610	100	[36]
[Ru(TzBA)(phen) ₂]	0.002	-	525	65	Our work
[Ru(TzBA)(phen)SCN]	0.004	-	619	80	Our work
[Ru(TzBA)(bpy) ₂]	0.005	-	602	105	Our work
[Ru(TzBA)(phen)(pyTz) SCN]	0.007	-	621	135	Our work
[Ru(TzBA)(bpy)(pyTz) SCN]	0.009	-	596	150	Our work

The relative ECL intensities (rECL-Int.) have been calculated by $rECL-Int.(%) = 100 * I_{ECL, MAX} / I_{ECL, MAX, Ru(bpy)_3^{2+}}$.

tpy:2,2':6', 2''-terpyridine

bpy: 2,2'-bipyridyl

2-TTH: 2-(1-H-tetrazole-5-yl)-thiophene

2-TBTH: 5-bromo-2-(1-H-tetrazole-5-yl)-thiophene

4-TBNH: 4-(1,H-tetrazole-5-yl)-benzonitrile

BTBH₂: Bis-1,4-(1,H-tetrazole-5-yl)-benzene

pyTz: 2-(1,H-tetrazol-5-yl)pyridine)

Pyr Tz: pyrazinyl-tetrazolate

bpyrTz : 2,3-bis(1,H-tetrazol-5-yl)-pyrazine

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