Electronic Supplementary Information

Synthesis, structural characterization and anion-, cation-, and solvent induced tuning of photophysical properties of a bimetallic Ru(II) complex: combined experimental and DFT/TDDFT investigation

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Tables for supporting information

Table S1 Selected calculated bond distances (Å) and angles (deg) for [(bpy)$_2$Ru(H$_2$PyIm Phen)Ru (bpy)$_2$](ClO$_4$)$_4$·4H$_2$O (**1**) and [(bpy)$_2$Ru(H$_2$PyImPhen) Ru(bpy)$_2$](ClO$_4$)$_4$· (**2**)

1						**2**					
	gas	soln		gas	soln		gas	soln		Gas	soln
Ru1-N5	2.1183	2.1136	Ru2-N1	2.1204	2.1133	Ru1-N5	2.1073	2.1104	Ru2-N1	2.1073	2.1104
Ru1-N6	2.1178	2.1117	Ru2-N2	2.1207	2.1121	Ru1-N6	2.1192	2.1129	Ru2-N2	2.1192	2.1129
Ru1-N7	2.1207	2.1121	Ru2-N3	2.1178	2.1117	Ru1-N7	2.1188	2.1141	Ru2-N3	2.1188	2.1141
Ru1-N8	2.1204	2.1133	Ru2-N4	2.1183	2.1136	Ru1-N8	2.1063	2.1113	Ru2-N4	2.1063	2.1113
Ru1-N9	2.1276	2.1194	Ru2-N16	2.1276	2.1194	Ru1-N9	2.1135	2.1180	Ru2-N16	2.1170	2.1189
Ru1-N10	2.1265	2.1202	Ru2-N17	2.1265	2.1202	Ru1-N10	2.1170	2.1189	Ru2-N17	2.1135	2.1180
Bond angles											
N5-Ru1-N6	77.54	77.66	N1-Ru2-N2	77.50	77.65	N5-Ru1-N6	77.52	77.64	N1-Ru2-N2	77.52	77.64
N5-Ru1-N7	96.87	97.38	N1-Ru2-N3	96.79	97.08	N5-Ru1-N7	99.06	97.64	N1-Ru2-N3	99.06	97.64
N5-Ru1-N8	172.24	172.94	N1-Ru2-N4	172.22	172.94	N5-Ru1-N8	175.29	173.47	N1-Ru2-N4	175.29	173.48
N5-Ru1-N9	89.04	88.05	N1-Ru2-N16	97.01	97.31	N5-Ru1-N9	87.71	88.42	N1-Ru2-N16	96.13	97.01
N5-Ru1-N10	97.64	97.16	N1-Ru2-N17	88.42	88.46	N5-Ru1-N10	96.14	97.10	N1-Ru2-N17	87.71	88.42
N6-Ru1-N7	88.27	88.86	N2-Ru2-N3	88.27	88.86	N6-Ru1-N7	89.44	89.04	N2-Ru2-N3	89.43	89.04
N6-Ru1-N8	96.79	97.08	N2-Ru2-N4	96.87	97.38	N6-Ru1-N8	99.05	97.66	N2-Ru2-N4	99.06	97.66
N6-Ru1-N9	97.25	96.64	N2-Ru2-N16	172.68	172.99	N6-Ru1-N9	95.84	96.57	N2-Ru2-N16	172.04	172.88
N6-Ru1-N10	173.39	172.96	N2-Ru2-N17	96.86	96.59	N6-Ru1-N10	172.04	172.88	N2-Ru2-N17	95.84	96.57
N7-Ru1-N8	77.50	77.65	N3-Ru2-N4	77.54	77.66	N7-Ru1-N8	77.55	77.62	N3-Ru2-N4	77.55	77.62
N7-Ru1-N9	172.68	172.99	N3-Ru2-N16	97.25	96.64	N7-Ru1-N9	172.20	172.52	N3-Ru2-N16	96.38	96.37
N7-Ru1-N10	96.86	96.59	N3-Ru2-N17	173.39	172.96	N7-Ru1-N10	96.37	96.37	N3-Ru2-N17	172.21	172.52
N8-Ru1-N9	97.01	97.31	N4-Ru2-N16	89.04	88.055	N8-Ru1-N9	95.90	96.66	N4-Ru2-N16	87.54	88.05
N8-Ru1-N10	88.41	88.46	N4-Ru2-N17	97.64	97.16	N8-Ru1-N10	87.54	88.05	N4-Ru2-N17	95.90	96.66
N9-Ru1-N10	77.10	78.28	N16-Ru2-N17	77.10	78.28	N9-Ru1-N10	78.95	78.47	N16-Ru2-N17	78.95	78.47

Table S2 Selected calculated bond distances (Å) and angles (deg) for **1·Zn**

1·Zn			
Ru1-N5	2.1137	Ru2-N1	2.1149
Ru1-N6	2.1124	Ru2-N2	2.1120
Ru1-N7	2.1120	Ru2-N3	2.1123
Ru1-N8	2.1149	Ru2-N4	2.1137
Ru1-N9	2.1170	Ru2-N16	2.1197
Ru1-N10	2.1197	Ru2-N17	2.1170
Zn-N13	2.1660	Zn-N12	2.3461
Zn-N15	2.3471		
N5-Ru1-N6	77.66	N1-Ru2-N2	77.66
N5-Ru1-N7	96.97	N1-Ru2-N3	97.01
N5-Ru1-N8	172.60	N1-Ru2-N4	172.60
N5-Ru1-N9	88.61	N1-Ru2-N16	88.80
N5-Ru1-N10	96.95	N1-Ru2-N17	97.16
N6-Ru1-N7	88.87	N2-Ru2-N3	88.87
N6-Ru1-N8	96.99	N2-Ru2-N4	96.97
N6-Ru1-N9	96.76	N2-Ru2-N16	96.70
N6-Ru1-N10	172.72	N2-Ru2-N17	172.81
N7-Ru1-N8	77.66	N3-Ru2-N4	77.66
N7-Ru1-N9	172.82	N3-Ru2-N16	172.72
N7-Ru1-N10	96.70	N3-Ru2-N17	96.77
N8-Ru1-N9	97.16	N4-Ru2-N16	96.94
N8-Ru1-N10	88.80	N4-Ru2-N17	88.62
N9-Ru1-N10	78.07	N16-Ru2-N17	78.07
N12-Zn-N13	74.39	N13-Zn-N15	74.37
		N12-Zn-N15	148.76

Table S3 Selected MOs along with their energies and compositions for **1·Zn**

MO	Energy, eV	(%) Composition			
	3	Ru^{II}	Zn^{II}	Ligand	bpy
HOMO-3	-6.634	79.62	0.02	10.57	9.79
HOMO-2	-6.623	77.23	0.01	13.26	9.49
HOMO-1	-6.491	84.82	0.00	5.32	9.85
HOMO	-6.491	84.81	0.00	5.34	9.85
LUMO	-3.232	0.33	2.24	93.13	4.30
LUMO+1	-3.116	1.51	0.02	92.80	5.67
LUMO+2	-2.998	4.57	1.09	78.81	15.52
LUMO+3	-2.967	3.29	0.17	79.47	17.07

Table S4 Photophysical data for **1** in binary solvent mixture

CH_2Cl_2 : DMF					H_2O : CH_3CN				
CH_2Cl_2 : DMF	τ [ns]	$\phi \times 10^{-1}$	$K_r \times 10^5$	$K_{nr} \times 10^6$	H_2O : CH_3CN	τ [ns]	$\phi \times 10^{-1}$	$K_r \times 10^5$	$K_{nr} \times 10^6$
10:0	410	1.10	2.68	2.17	10:0	500	1.14	2.28	1.77
9:1	397	1.08	2.72	2.25	9:1	437	0.95	2.17	2.07
8:2	344	0.98	2.85	2.62	8:2	352	0.92	2.61	2.58
7:3	323	0.88	2.72	2.82	7:3	240	0.71	2.96	3.87
6:4	293	0.74	2.53	3.16	6:4	225	0.59	2.62	4.18
5:5	280	0.69	2.46	3.33	5:5	205	0.55	2.68	4.61
4:6	264	0.62	2.35	3.55	4:6	190	0.50	2.63	5.00
3:7	237	0.57	2.41	3.98	3:7	181	0.45	2.49	5.28
2:8	225	0.53	2.36	4.21	2:8	171	0.43	2.51	5.60
1:9	208	0.49	2.40	4.66	1:9	165	0.41	2.48	5.81
0:10	202	0.42	2.09	4.74	0:10	163	0.40	2.42	5.89

Figures for Electronic Supplementary Information

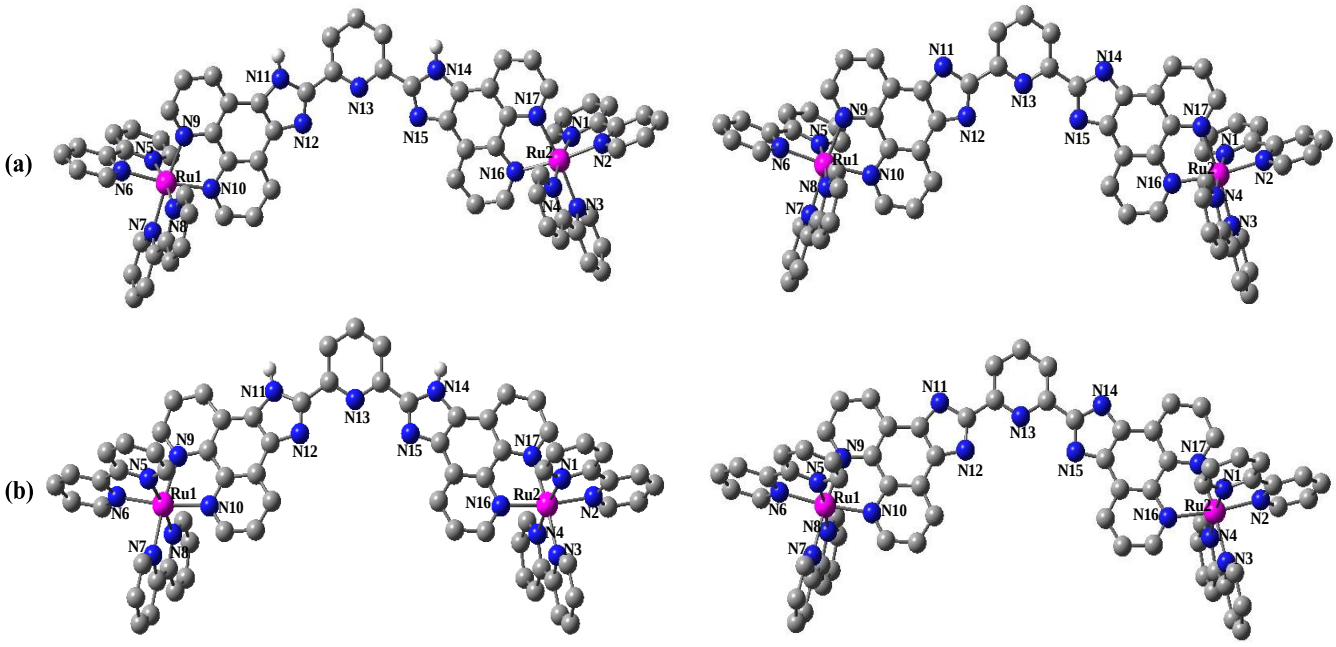

Fig. S1 Optimized geometries and labeling schemes of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) and $[(bpy)_2Ru(PyImPhen)Ru(bpy)_2](ClO_4)_2$ (**2**) in gas (a) and solution phase (b).

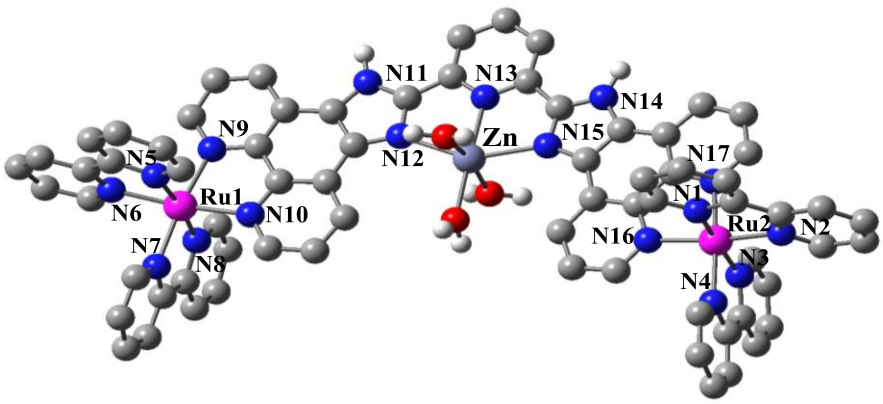

Fig. S2 Optimized geometries and labeling schemes of **1·Zn** in solution phase.

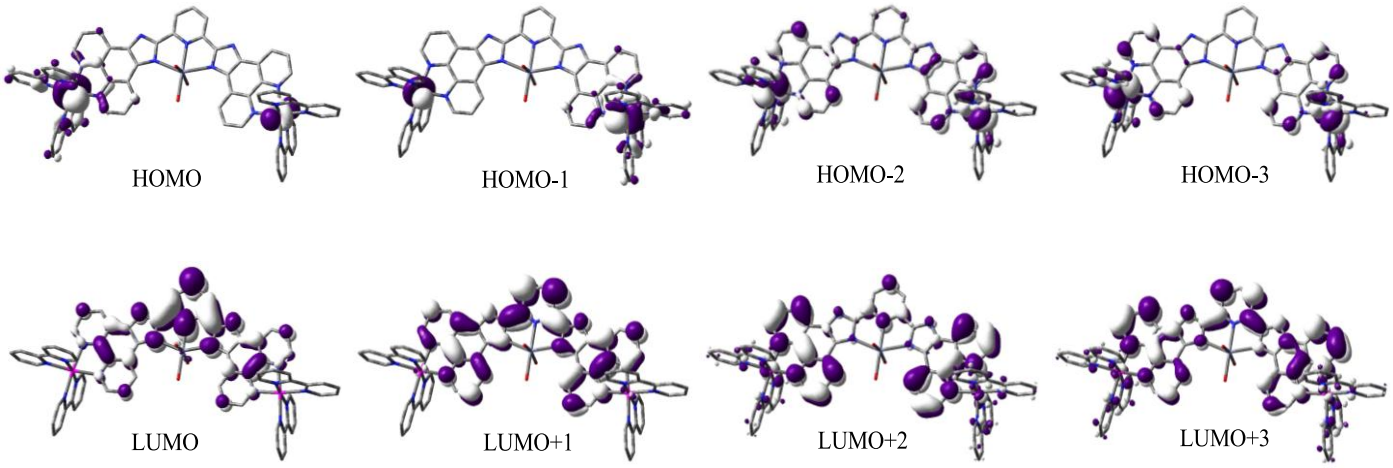

Fig. S3 Schematic drawings of the selective frontier molecular orbitals for **1·Zn** in solution phase.

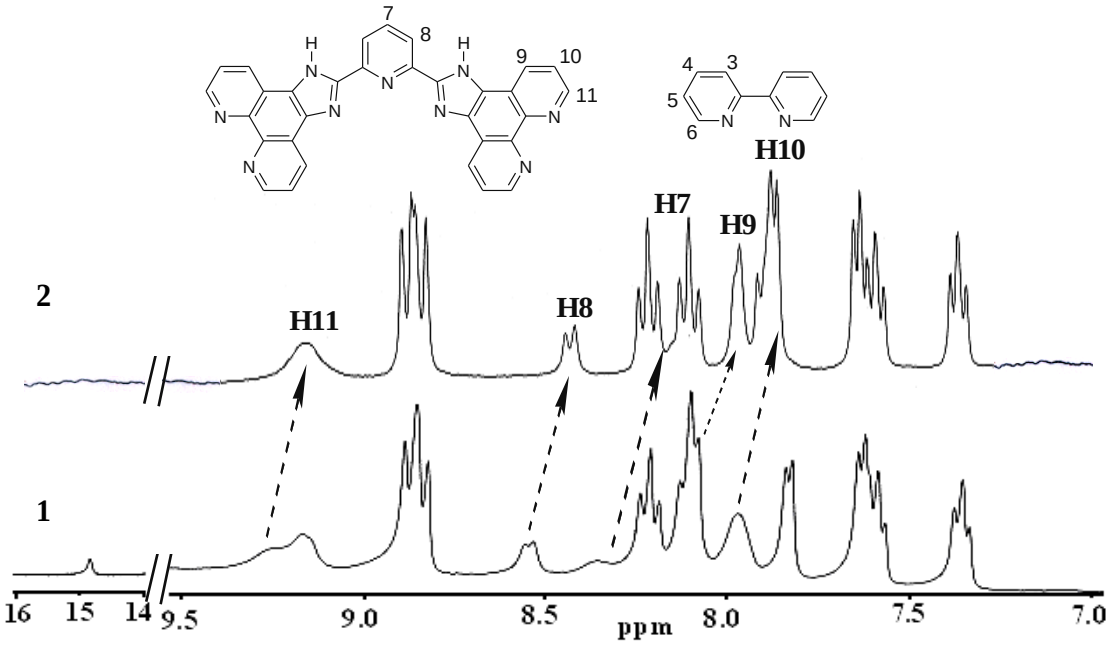

Fig. S4 ^{1}H spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) (below) and $[(bpy)_2Ru(PyImPhen)Ru(bpy)_2](ClO_4)_2$ (**2**) (above) in DMSO-d_6.

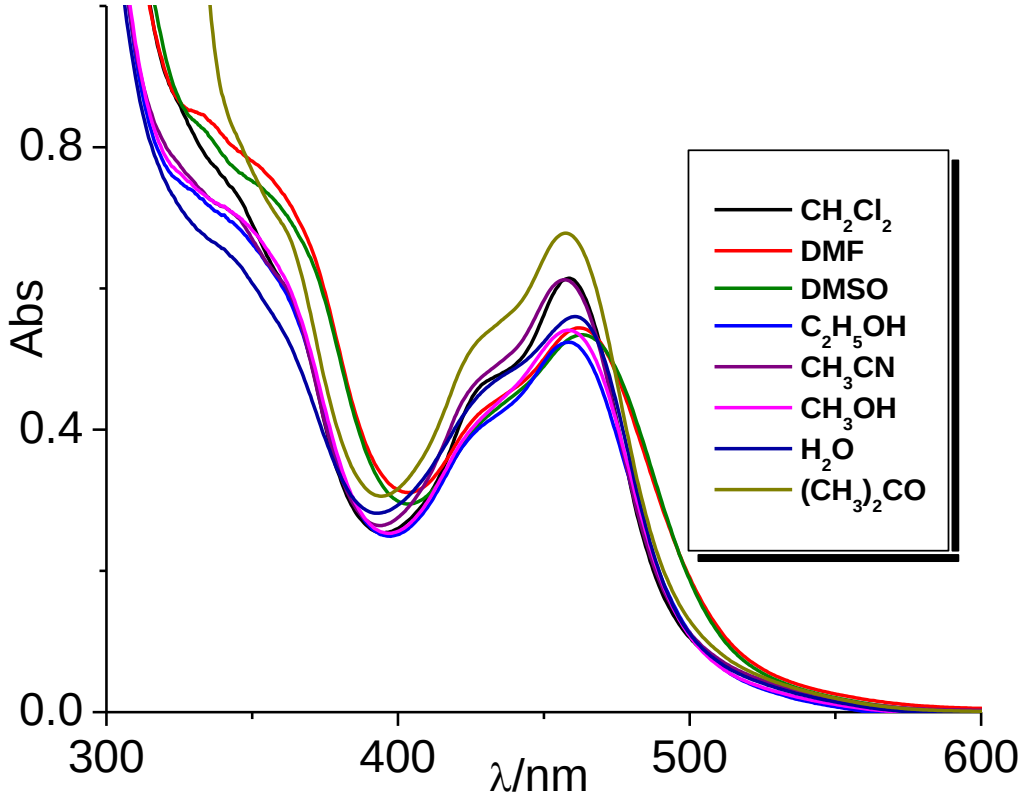

Fig. S5 UV-vis spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in different solvents.

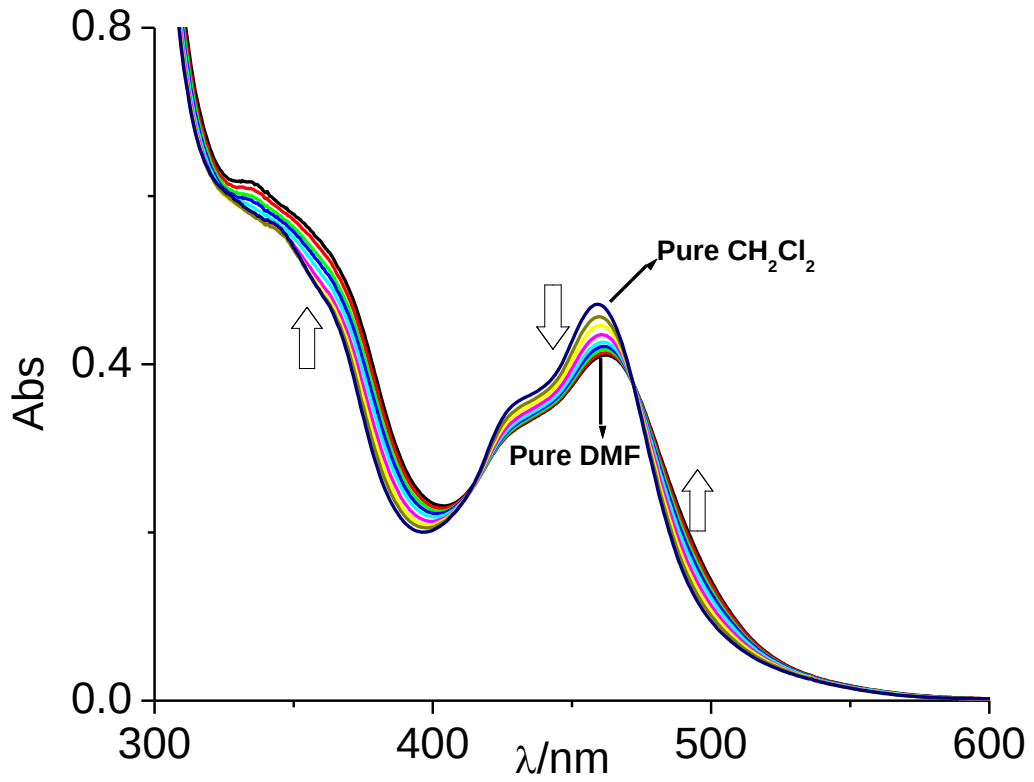

Fig. S6 Changes in UV-vis spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) on incremental addition of DMF in CH_2Cl_2.

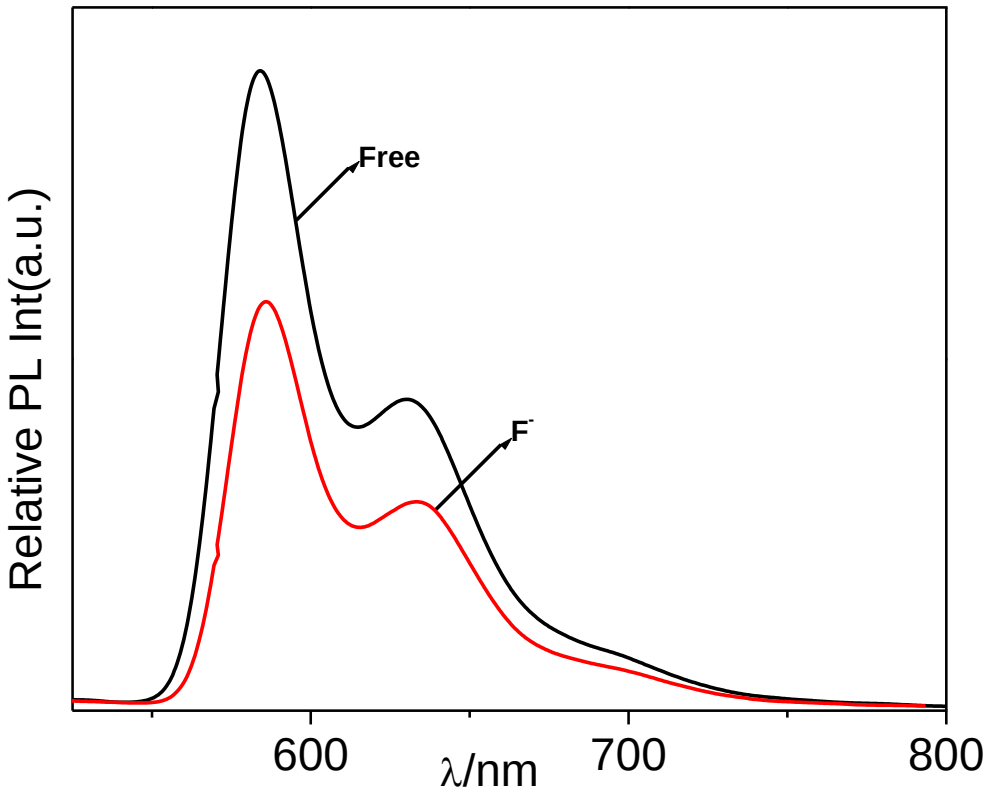

Fig. S7 Luminescence spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2]$ $(ClO_4)_4 \cdot 4H_2O$ (**1**) in presence (red line) and in absence (black line) of F^- at 77 K in 4:1 ethanol–methanol glass.

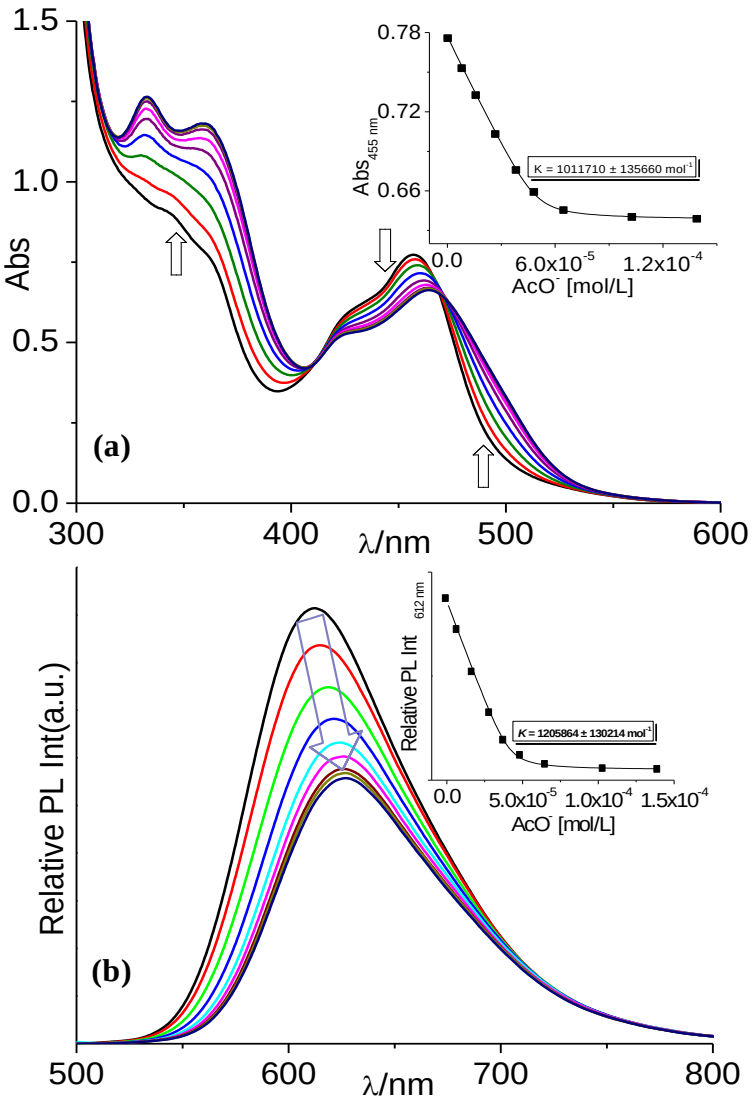

Fig. S8 Changes in UV-vis (a) and photoluminescence (b) spectra of $[(bpy)_2Ru(H_2PyIm\ Phen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in acetonitrile upon addition of AcO^- ion. Inset shows the fit of the experimental emission data to a 1:1 binding profile.

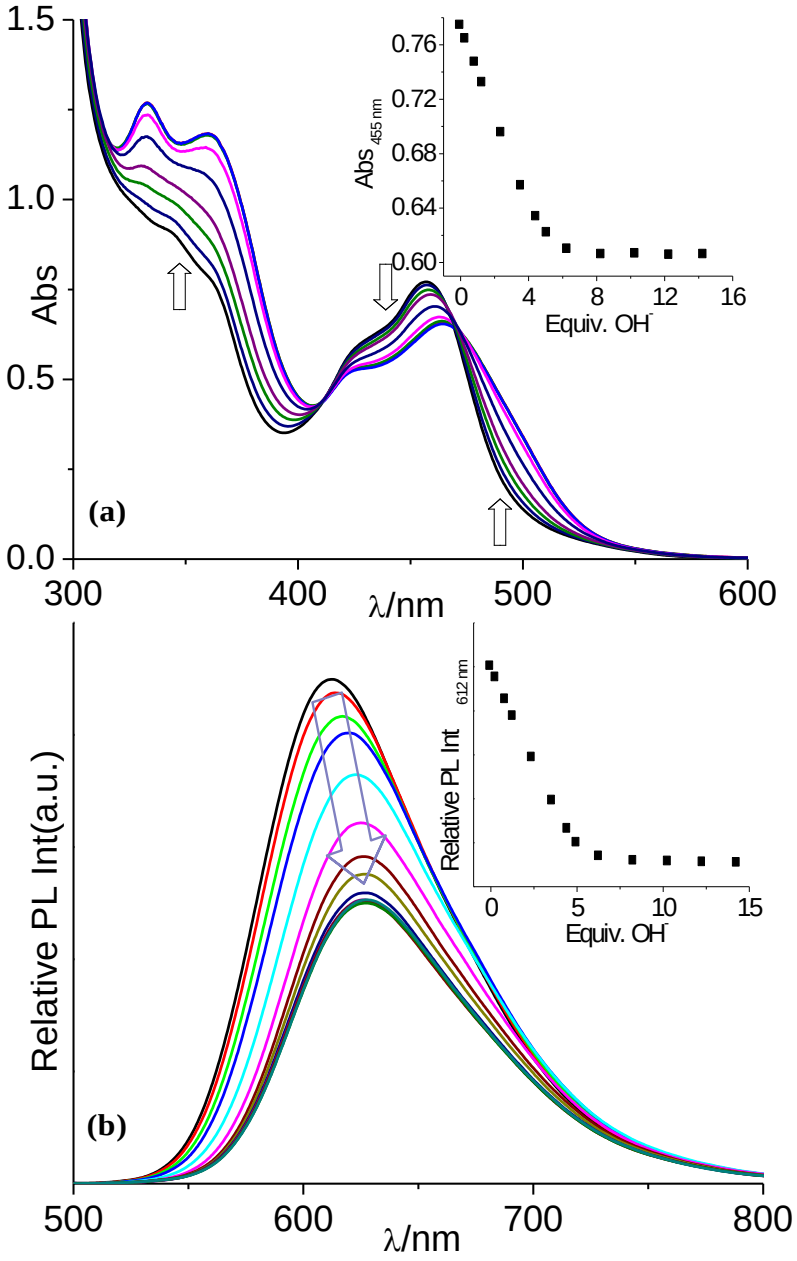

Fig. S9 Changes in UV-vis (a) and photoluminescence (b) spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in acetonitrile upon addition of OH^- ion. The inset shows the change of absorption and emission intensity as a function of the equivalent of OH^- ion added.

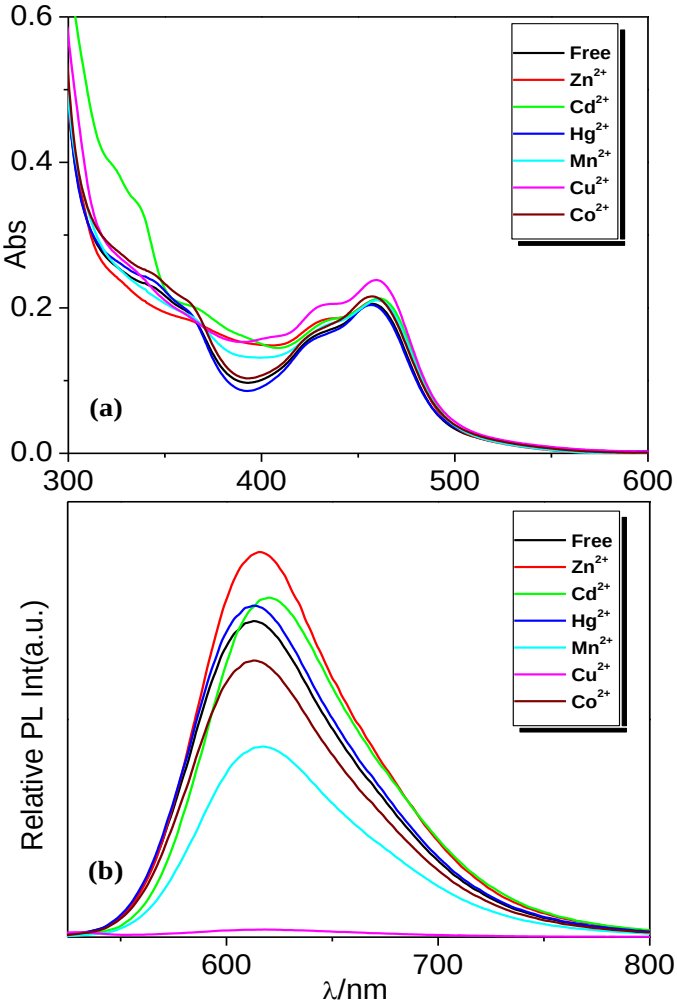

Fig. S10 Changes in UV-vis (a) and photoluminescence (b) spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in acetonitrile upon addition of different cations as perchlorate salts.

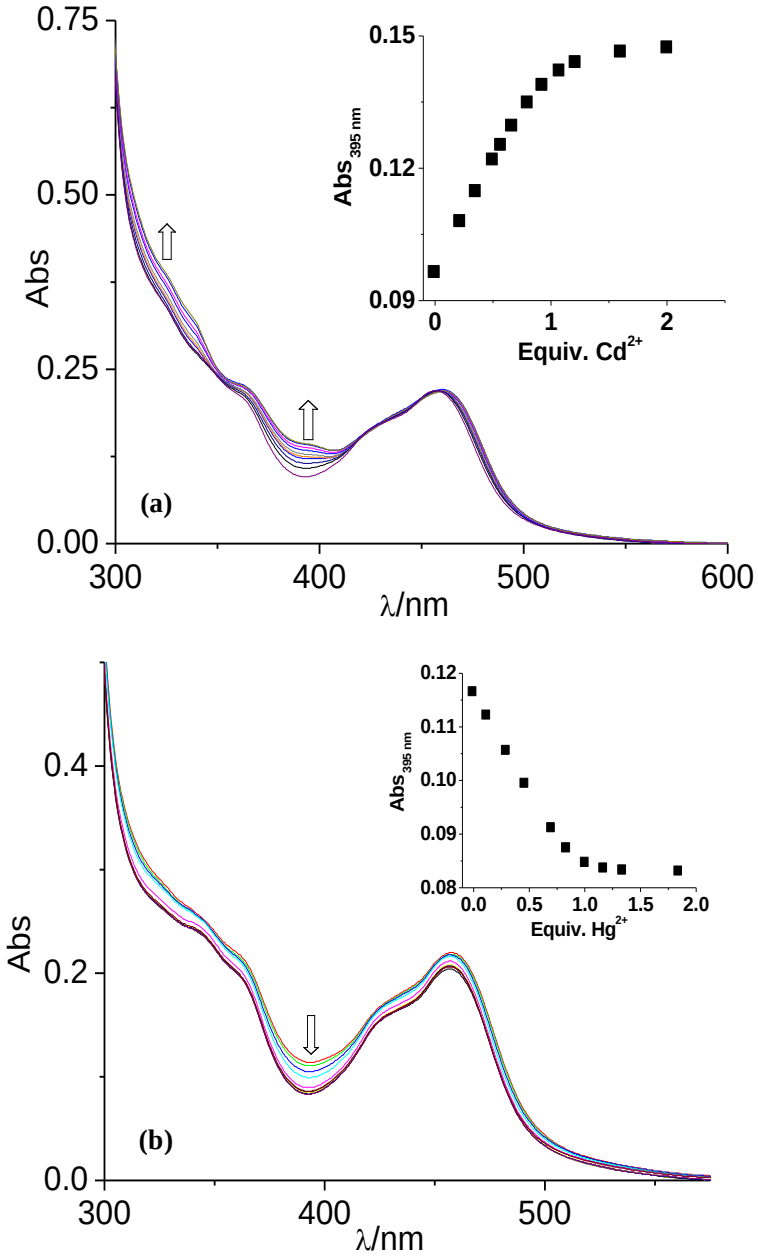

Fig. S11 Changes in UV-vis spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in acetonitrile upon addition of Cd^{2+} (a) and Hg^{2+} (b). The inset shows the change of absorption and emission intensity as a function of the equivalent of Cd^{2+} and Hg^{2+} ions added.

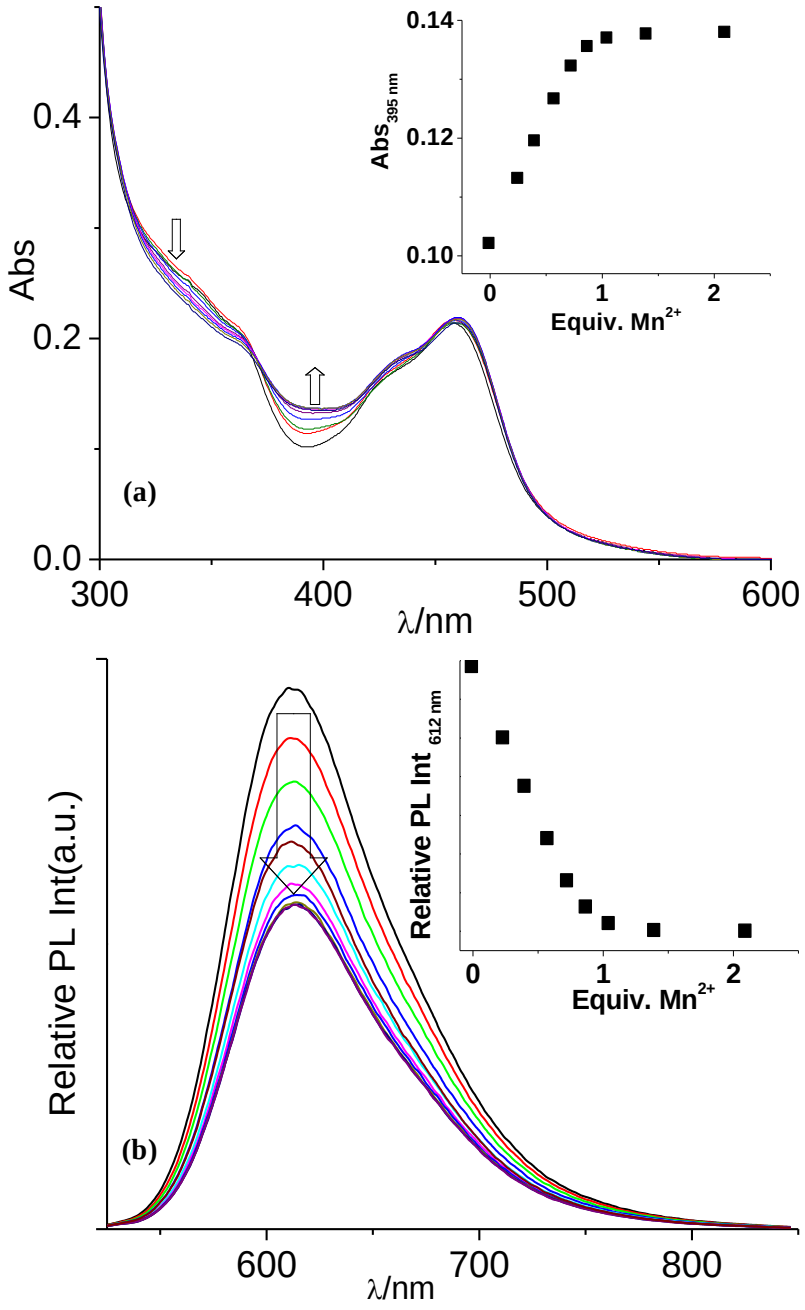

Fig. S12 Changes in UV-vis (a) and photoluminescence (b) spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in acetonitrile upon addition of $Mn(ClO_4)_2$. The inset shows the change of absorption and emission intensity as a function of the equivalent of Mn^{2+} ions added.

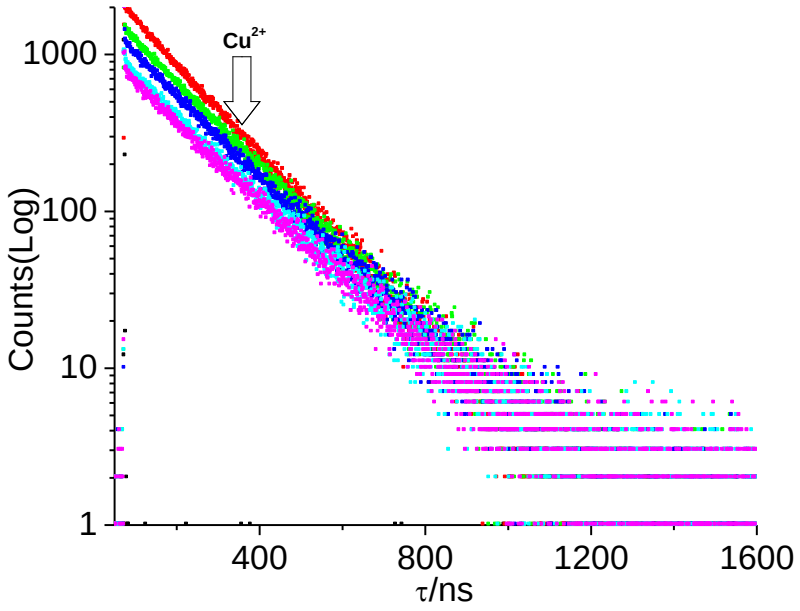

Fig. S13 Changes in time-resolved decay profiles of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in acetonitrile as function of the incremental addition of Cu^{2+}.

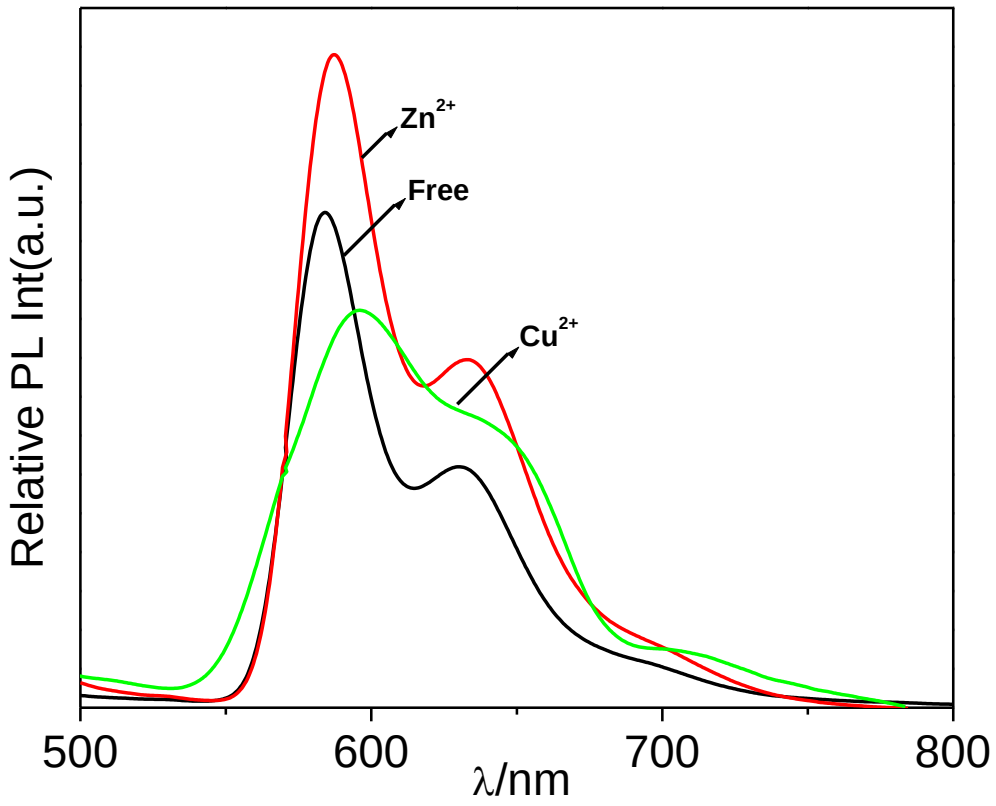

Fig. S14 Photoluminescence spectra of $[(bpy)_2Ru(H_2PyImPhen)Ru(bpy)_2](ClO_4)_4 \cdot 4H_2O$ (**1**) in absence (black line) and in presence of Zn^{2+} (red line) and Cu^{2+} (green) ions in ethanol-methanol (4:1) glass at 77 K.

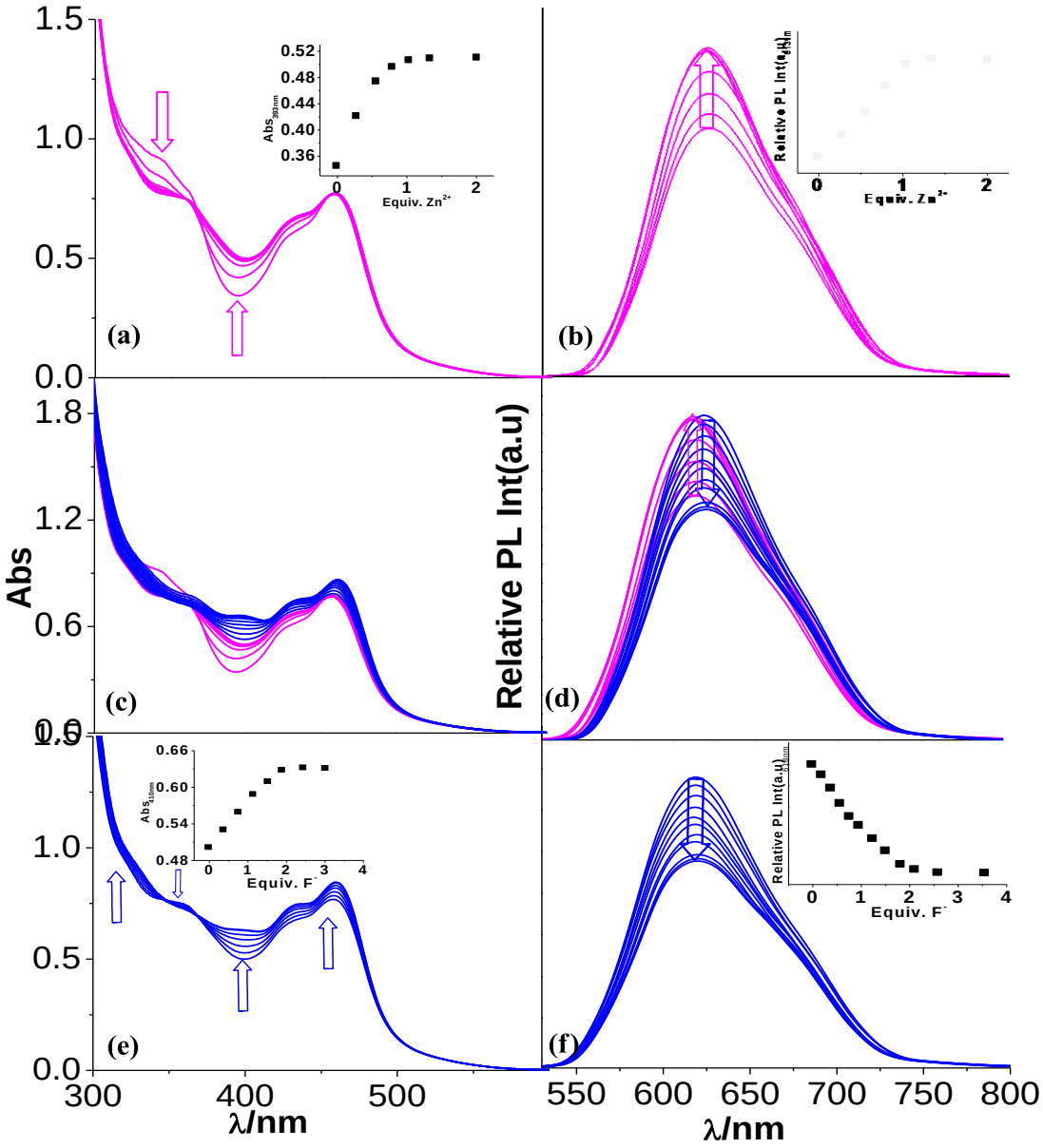

Fig. S15 Changes in UV-vis (a,c,e) and photoluminescence (b,d,f) spectra of **1** upon sequential incremental addition of Zn^{2+} and F^- ions in acetonitrile.