Supporting Information

Benzimidazole functionalized ancillary ligands for heteroleptic Ru(II) complexes: synthesis, characterization and dye-sensitized solar cell applications

*Tejaswi Jella,[a] Malladi Srikanth[b] Rambabu Bolligarla[a] Yarasi Soujanya,[b] Surya Prakash Singh[a] and Lingamallu Giribabu[a]**

*[a]Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad-500007, Telangana, India.

*[b]Center for Molecular Modeling, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad-500007, Telangana, India.

	Table of Contents	Page No.

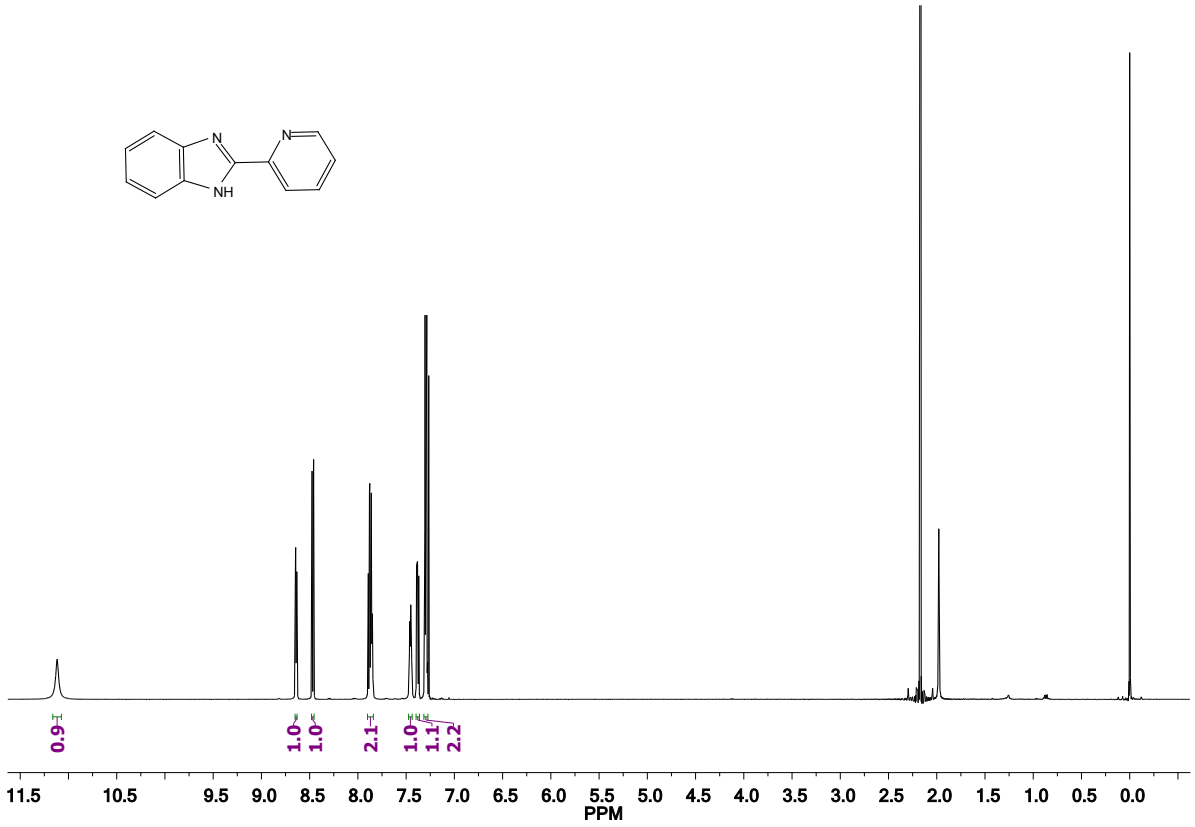

Figure S1.^{1}HNMR spectrum of 2-(pyridin-2-yl)-1H-benzimidazole.

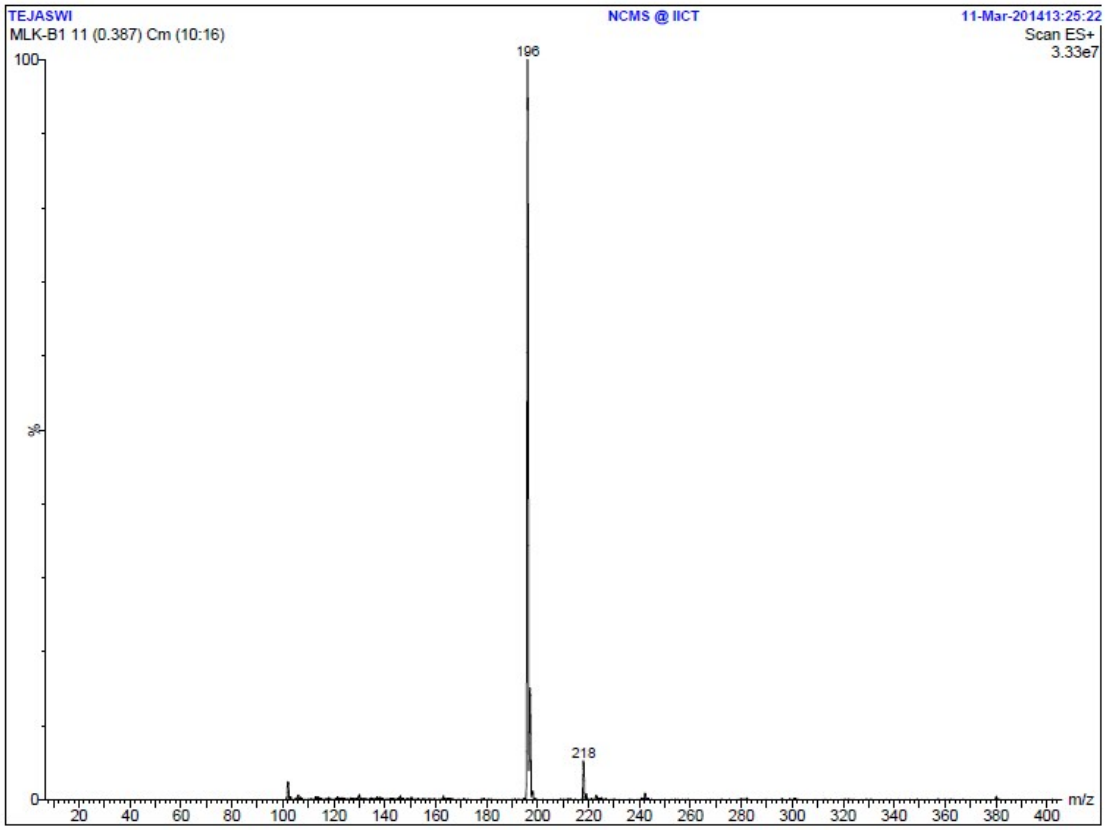

Figure S2. ESI-MS spectrum of 2-(pyridin-2-yl)-1H-benzimidazole.

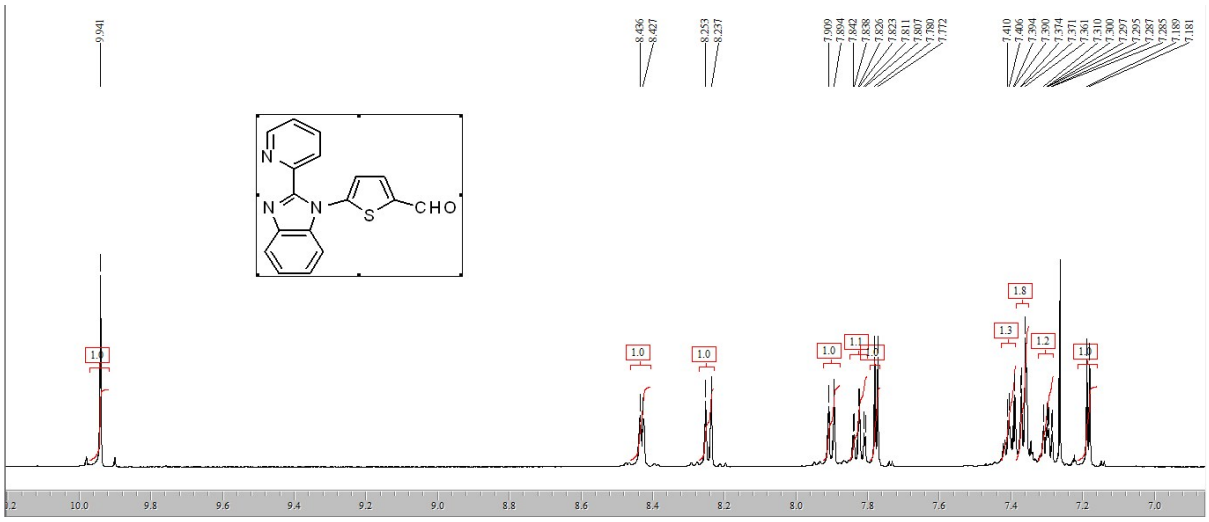

Figure S3.[1]HNMR spectrum of compound **PBI-S-CHO**.

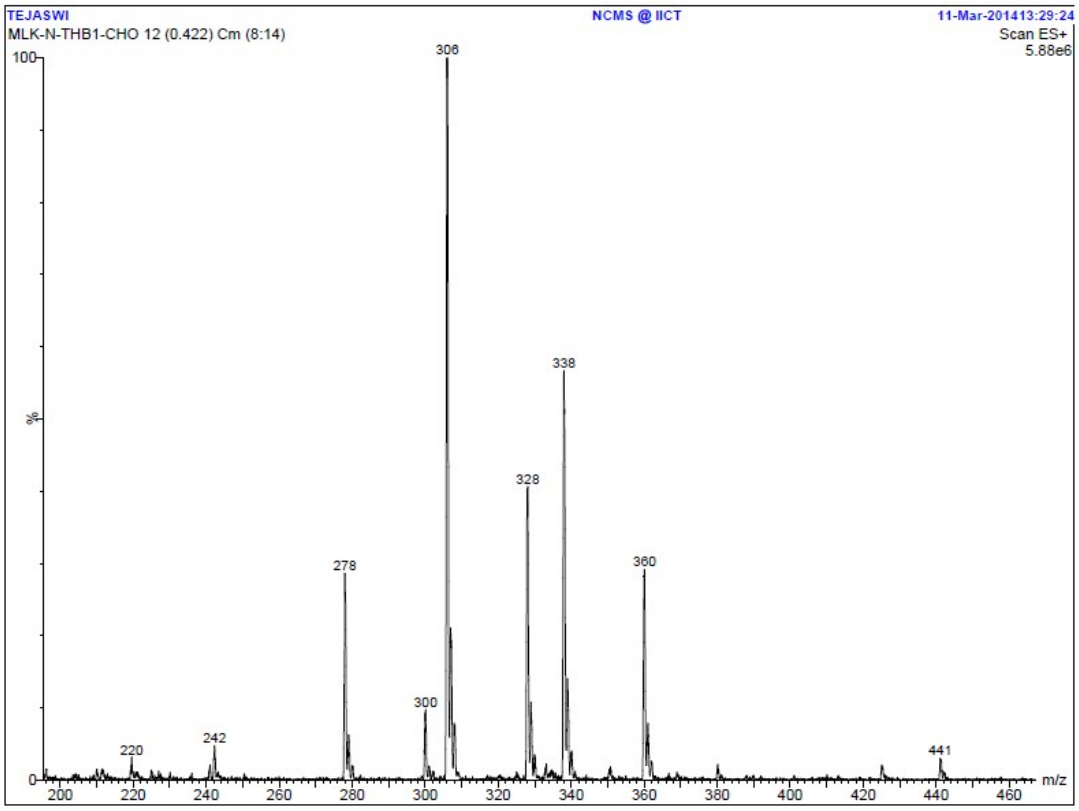

Figure S4. ESI-MS spectrum of compound **PBI-S-CHO**.

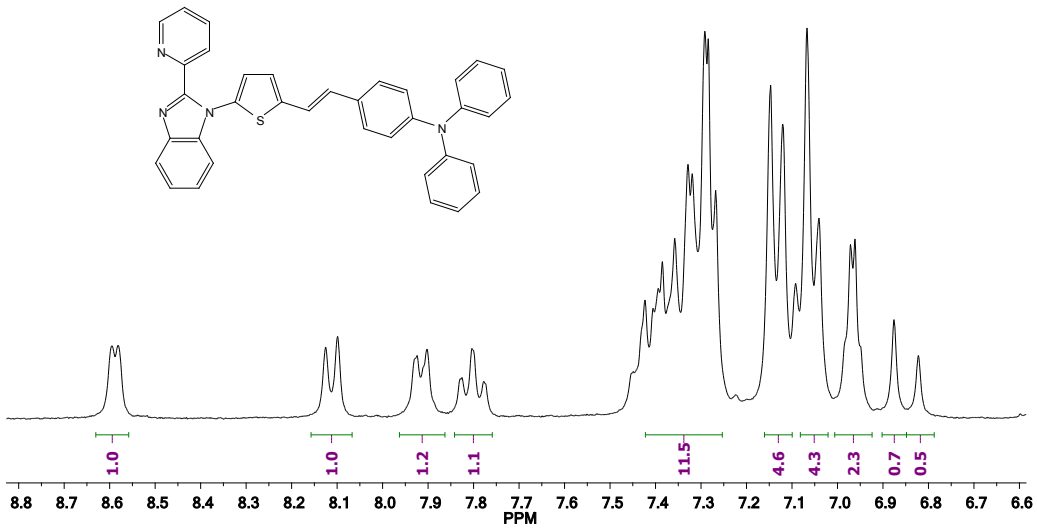

Figure S5.[1]HNMR spectrum of **L1**.

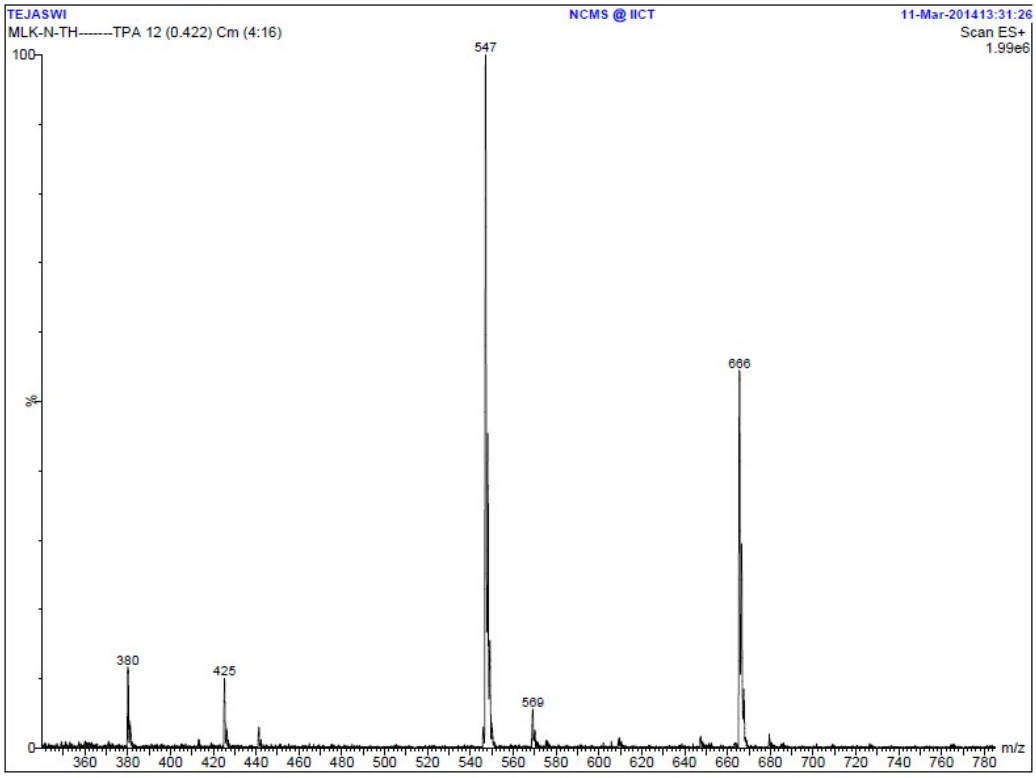

Figure S6. ESI-MS spectrum of **L1**.

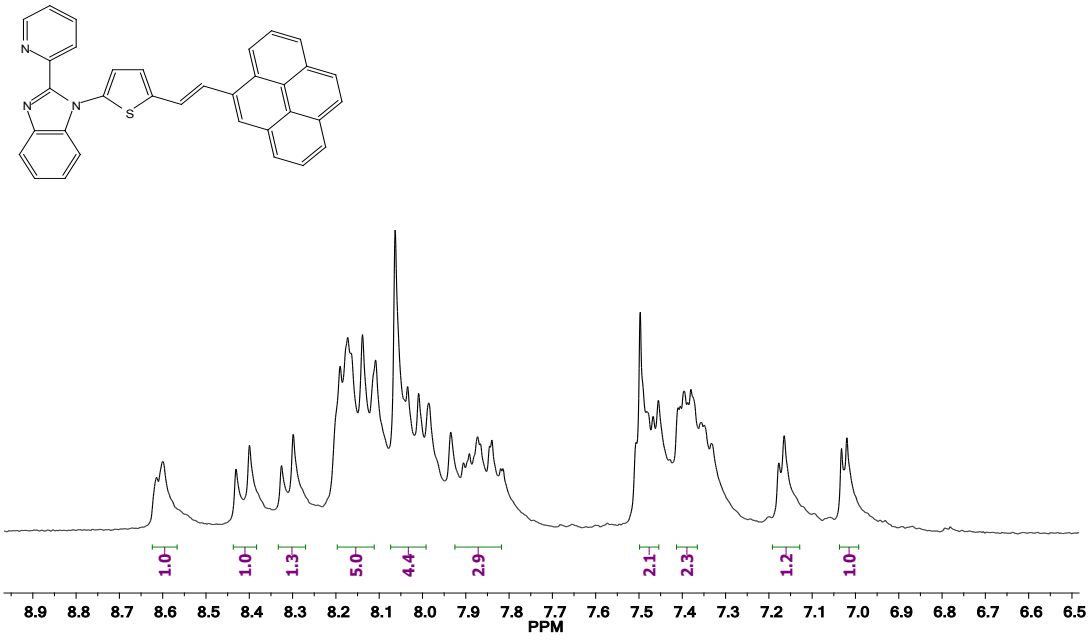

Figure S7. ^{1}HNMR spectrum of **L2**.

Figure S8. ESI-MS spectrum of **L2**.

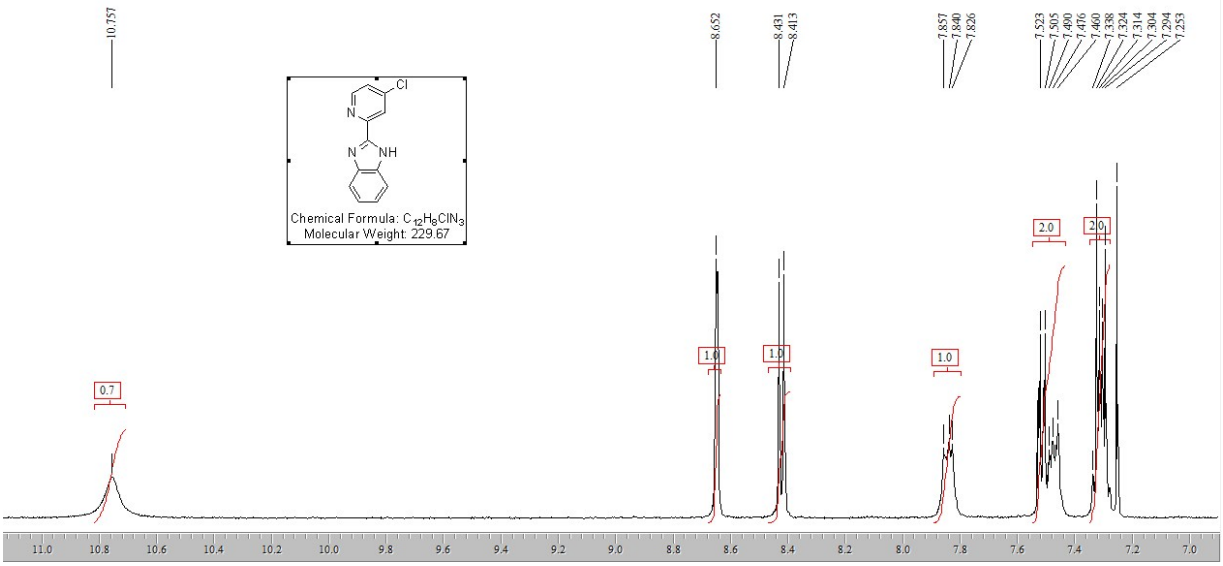

Figure S9. [1]HNMR spectrum of 2-(4-chloropyridin-2-yl)-1H-benzimidazole.

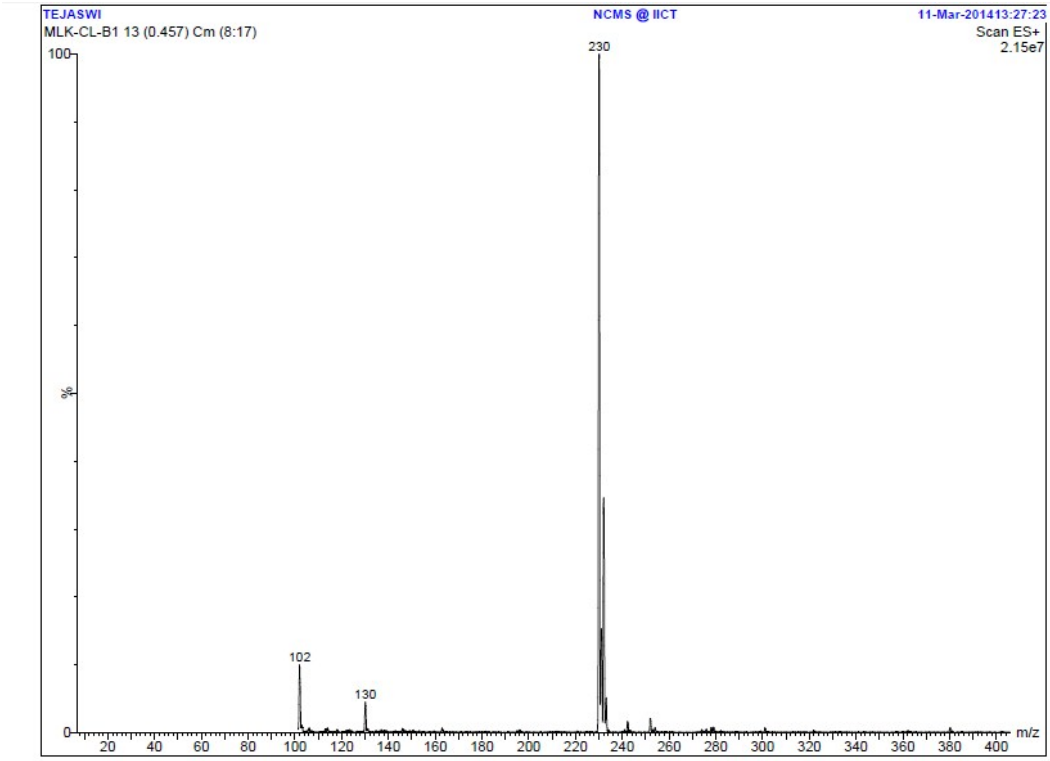

Figure S10. ESI-MS spectrum of 2-(4-chloropyridin-2-yl)-1H-benzimidazole.

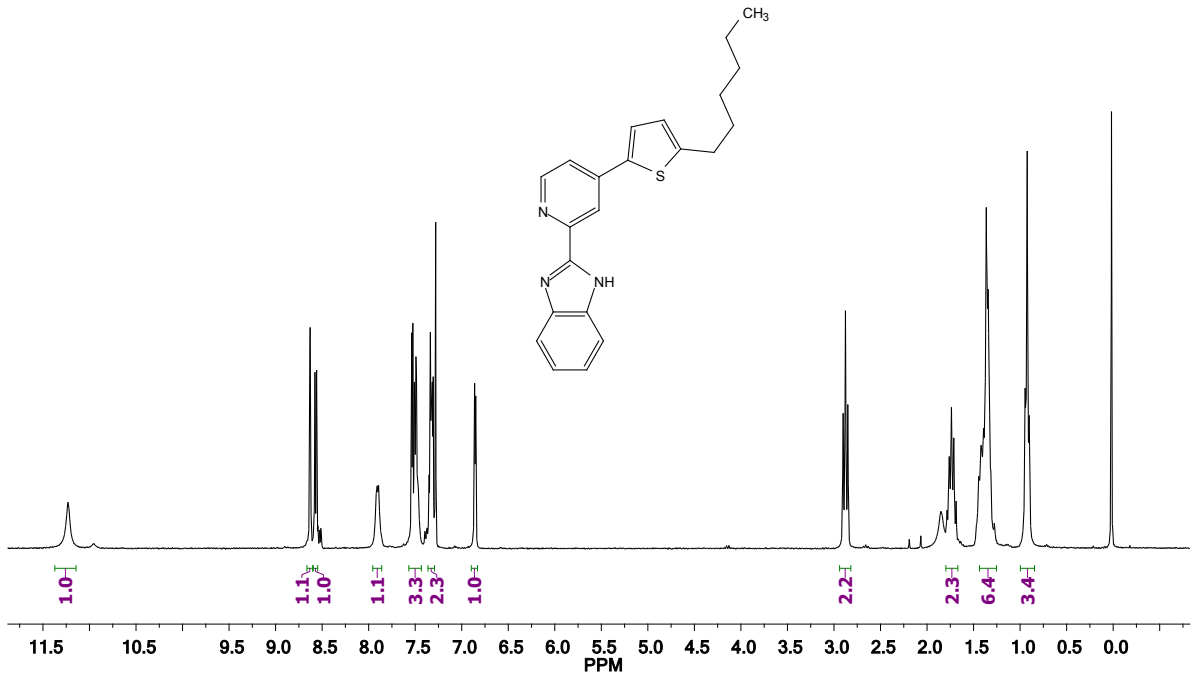

Figure S11. ^{1}H NMR spectrum of **P-BI-S-NH**.

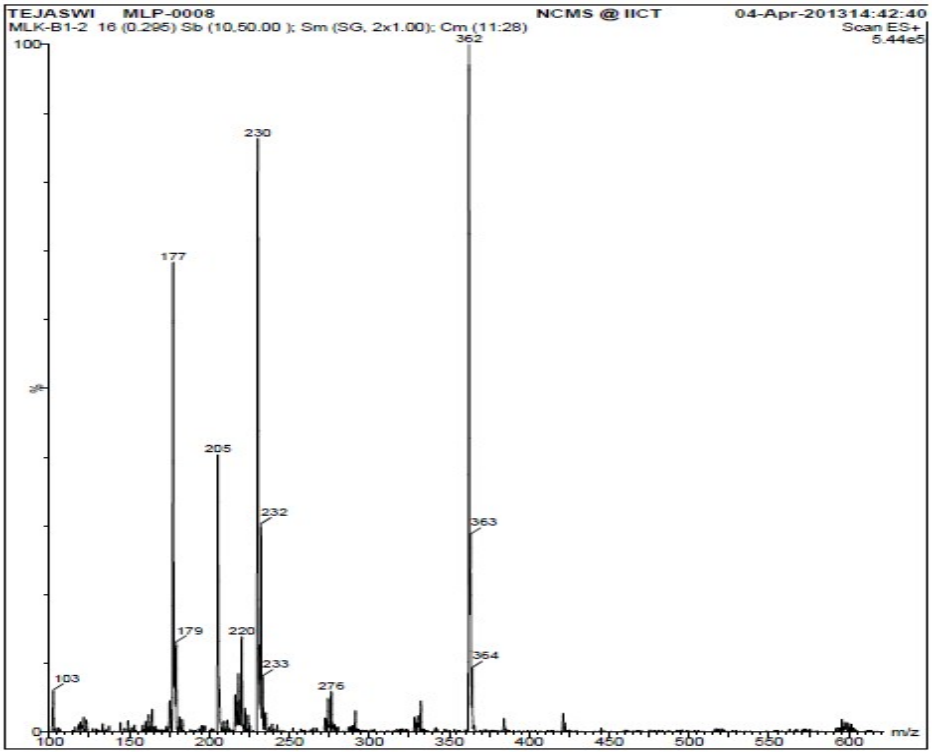

Figure S12. ESI-MS spectrum of compound **P-BI-S-NH**.

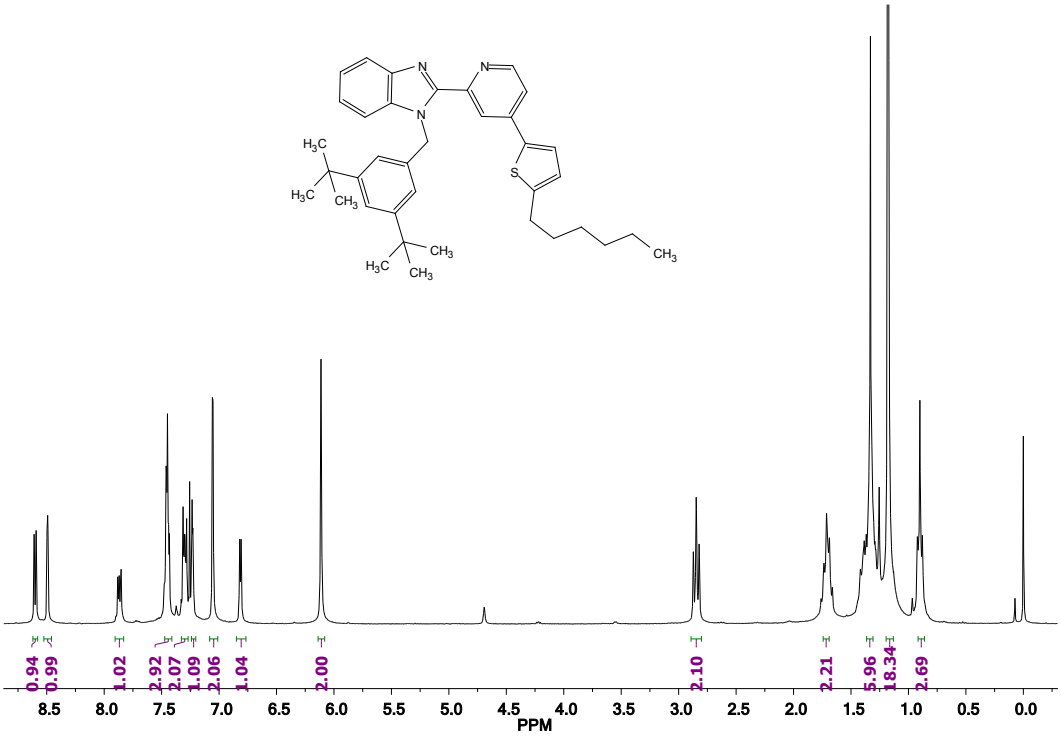

Figure S13. ^{1}H NMR spectrum of **L3**.

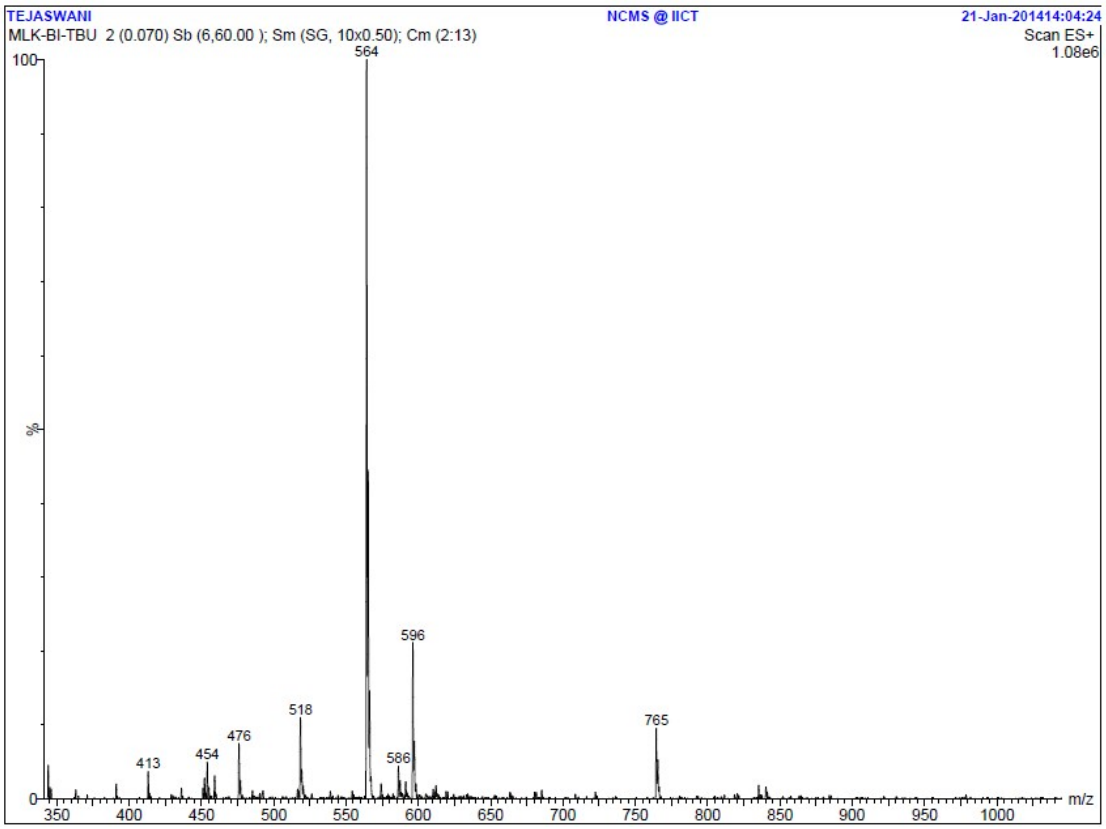

Figure S14. ESI-MS spectrum of **L3**.

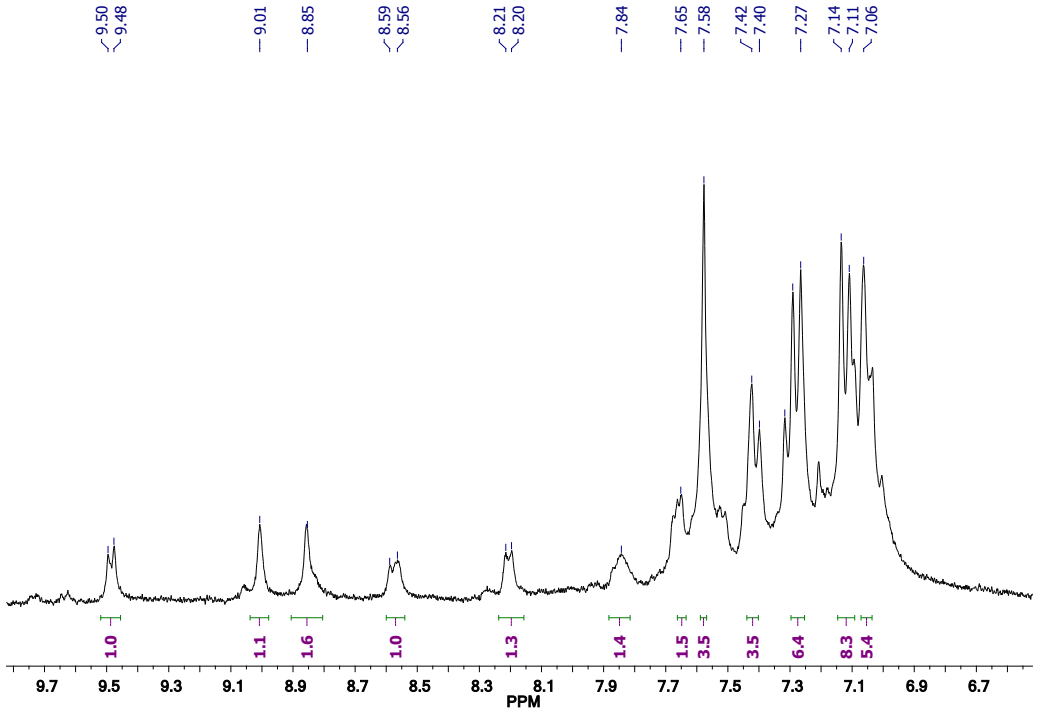

Figure S15. ^{1}H NMR spectrum of complex **1**.

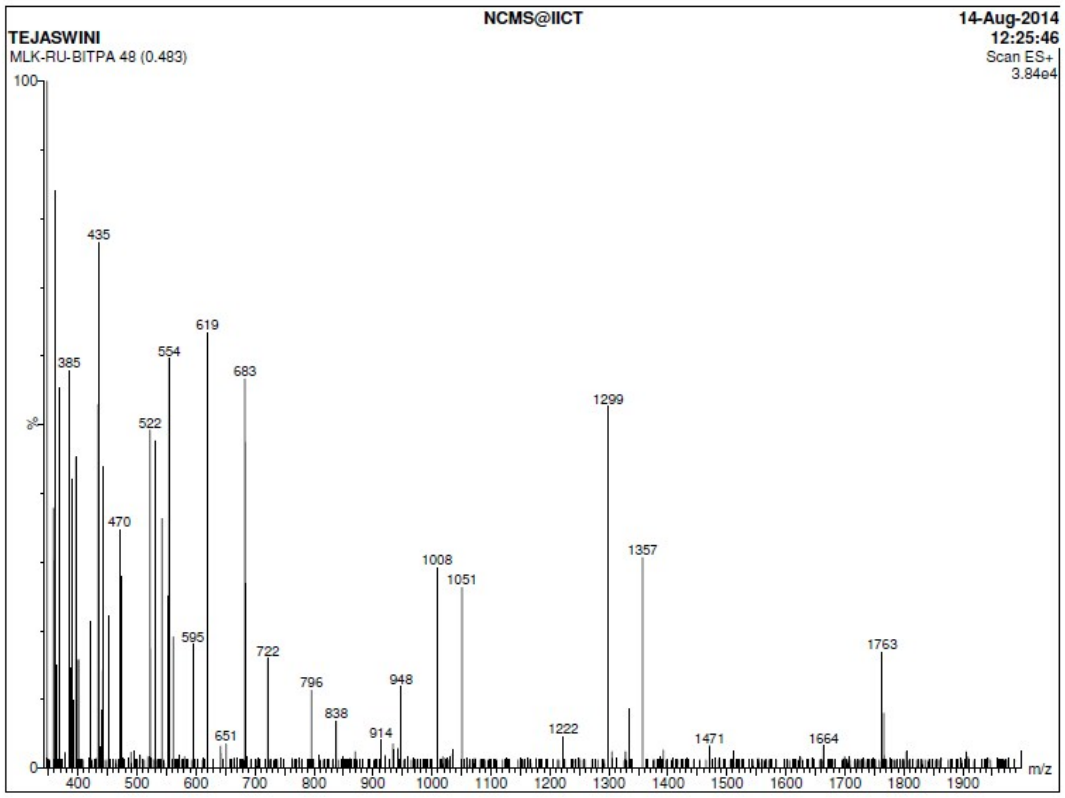

Figure S16. ESI-MS spectrum of complex **1**

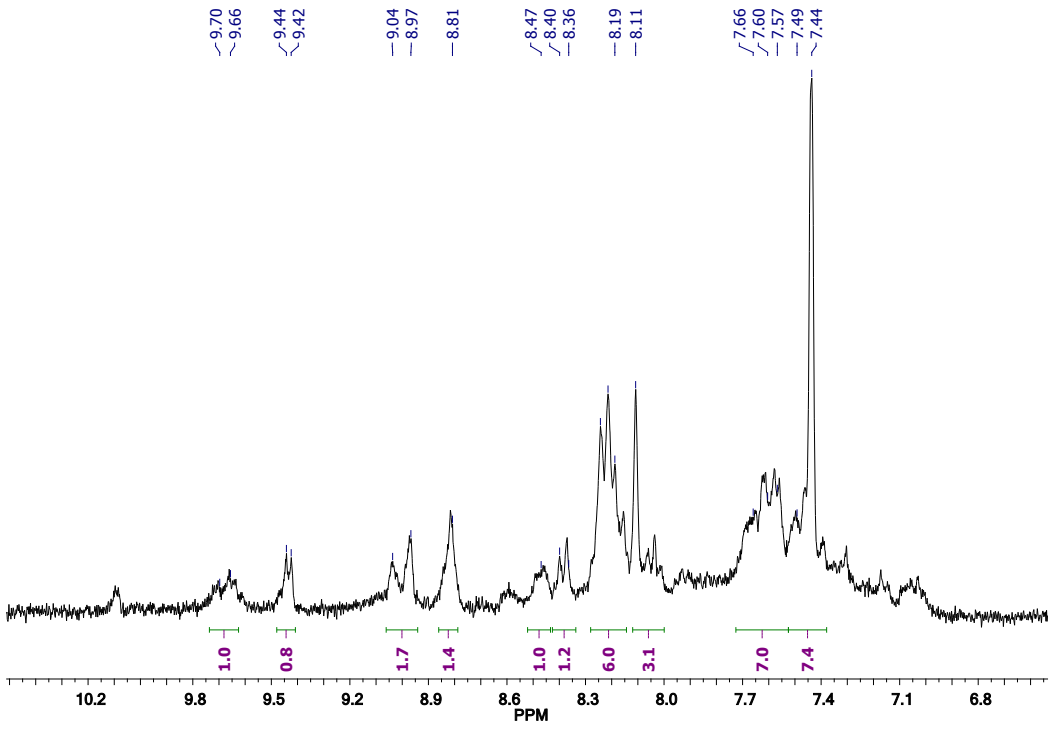

Figure S17. ^{1}H NMR spectrum of complex **2**.

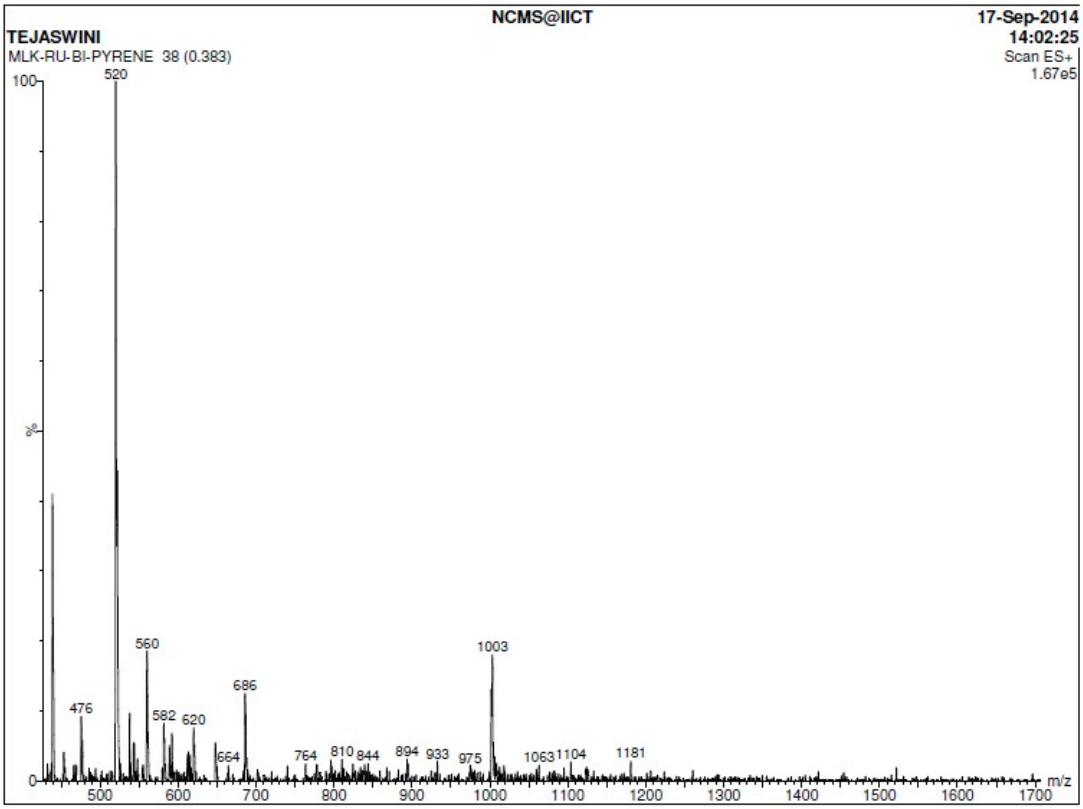

Figure S18. ESI-MS spectrum of complex **2**.

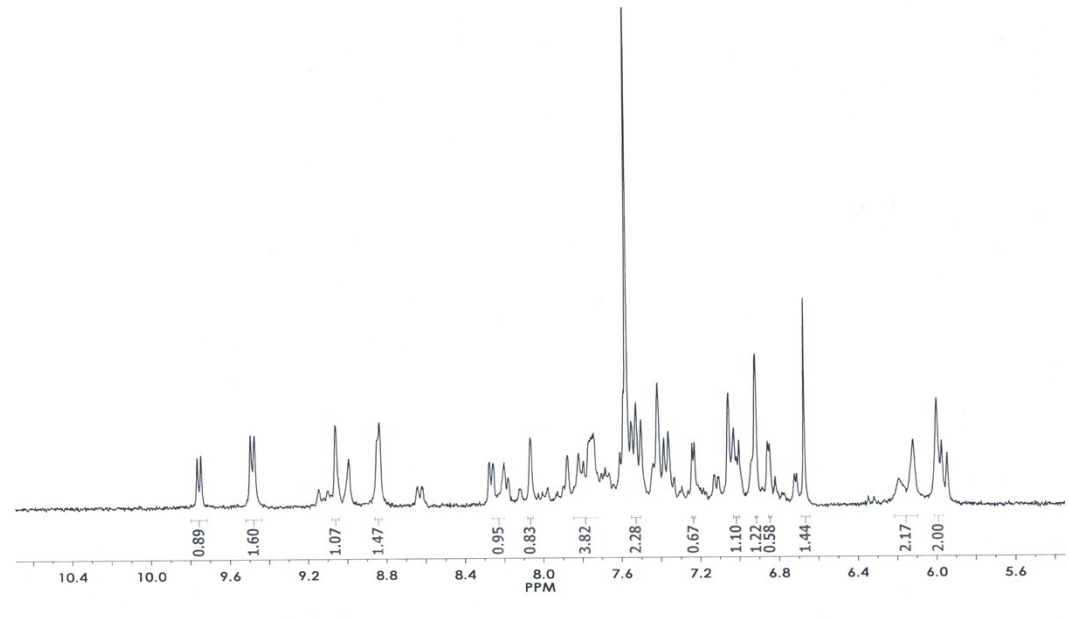

Figure S19. ^{1}H NMR spectrum of complex **3**.

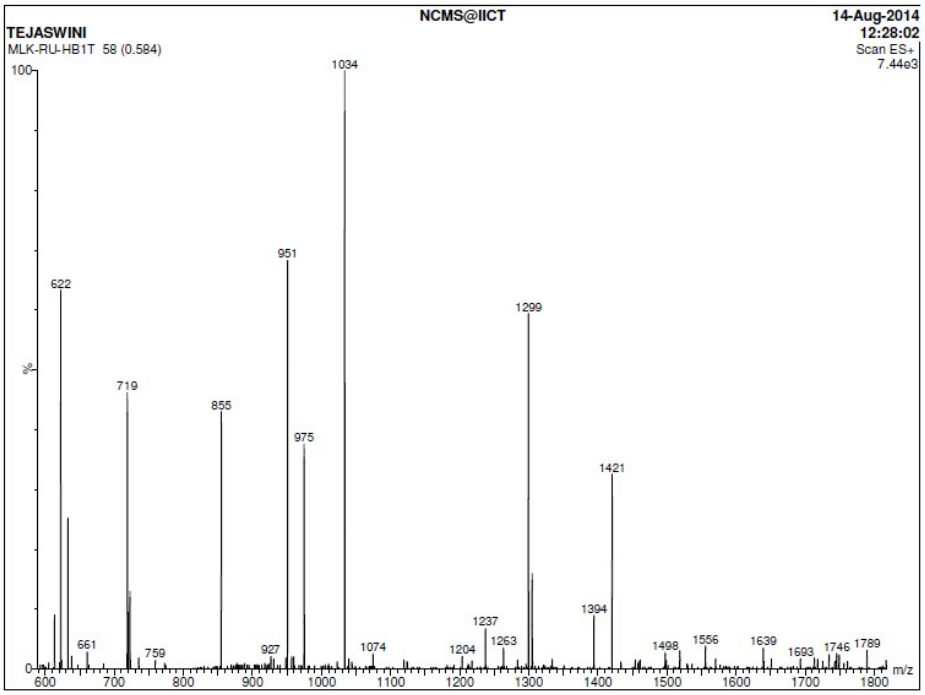

Figure S20. ESI-MS spectrum of complex **3**.

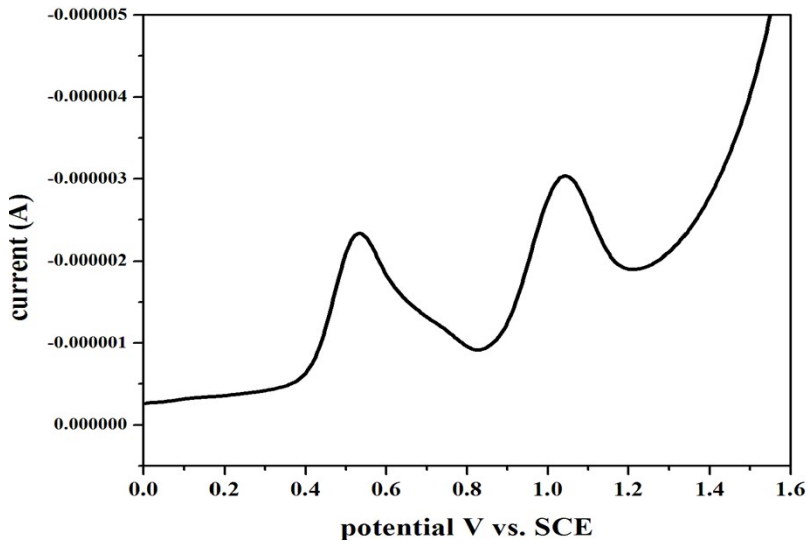

Figure S21. Differential pulse voltammogramme of complex **3**.

Table S1: Molecular orbital composition (in %) calculated at CAM-B3LYP/6-311+G(d,p):LanL2DZ// PBE/6-311+G(d,p):LanL2DZ.

System	orbital	Ru	NCS	Bpy	pyridine-BI
	HOMO-1	50	36	6	7
1	HOMO	0	0	0	100
	LUMO	6	1	93	0
	LUMO+1	3	0	1	94
	HOMO-1	51	37	5	7
2	HOMO	0	0	0	100
	LUMO	6	1	93	0
	LUMO+1	0	0	0	100
	HOMO-1	50	35	3	12
3	HOMO	52	36	5	7
	LUMO	6	1	93	0
	LUMO+1	3	0	1	96

Table S2: Calculated excited state energies (eV), absorption spectra wavelengths (nm), oscillator strengths (*f*), the major transition configurations (CI) is given for transitions > 5% at TD-CAM-B3LYP/6-311+G(d,p):LanL2DZ in acetonitrile solvent using C-PCM solvation.

Molecule	*E*/eV	λ	*f*	State	Major contribution MOs	Assignment
1	1.7256	687	0.0	T1	H-4→L+3 (37%), HOMO→L+3 (55%)	TPA(intra ligand)
	2.3370	530	0.0372	S1	H-1→LUMO (80%), H-3→LUMO (5%), H-2→LUMO (5%)	TPA→Bpy
	3.3106	374	0.9591	S7	HOMO→L+3 (70%), H-4→L+3 (6%), H-3→L+1 (9%)	TPA(intra ligand), Ru/NCS→BI
	4.3087	287	0.3019	S23	H-8→LUMO (34%), H-6→L+1 (21%), H-9→L+1 (11%), H-15→LUMO (6%), H-5→L+1 (5%), HOMO→L+6 (5%)	Ru/NCS/BI→Bpy, Ru/NCS/BI→ Ru/BI
2	1.4283	813	0.0	T1	HOMO→L+1 (74%),H-5→L+5 (10%)	Pyrene (intra ligand)
	2.3422	529	0.0386	S1	H-1→LUMO (80%), H-3→LUMO (5%)	Pyrene→Bpy
	3.1501	393	1.3803	S5	HOMO→L+1 (73%), H-2→L+2 (13%)	Pyrene (intra ligand), Ru/NCS→ Ru/BI
	4.1971	295	0.3704	S20	HOMO→L+5 (48%), H-5→L+1 (19%), H-1→L+6 (16%),	Pyrene (intra ligand), Pyrene→BI
3	2.0094	617	0.0	T1	HOMO→LUMO (78%), H-11→LUMO (5%)	Ru/NCS→Bpy
	2.3046	538	0.0361	S1	HOMO→LUMO (81%), H-2→LUMO (9%)	Ru/NCS→Bpy
	2.7700	447	0.1961	S3	H-2→LUMO (36%), HOMO→L+1 (40%)	Ru/NCS→Bpy, Ru/NCS→BI
	3.4112	363	0.1652	S7	HOMO→L+2 (70%), H-1→L+1 (10%)	Ru/NCS→Bpy ,Ru/NCS→BI
	3.7625	310	0.3335	S14	H-4→L+1 (15%), H-1→L+4 (14%), H-4→L+4 (5%), H-2→L+16 (8%), H-2→L+18 (6%), HOMO→L+4 (6%)	Ru/BI/NCS→Ru/BI, Ru/NCS→BI