Novel 4'- Functionalized 4, 4''-Dicarboxyterpyridine Ligands for Ruthenium Complexes: Near-IR Sensitization in Dye Sensitized Solar Cells.

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Table S1. Dihedral angles of **MC113-117** calculated at PBE0/LANL2DZ level, level of theory.

Dihedral angles *(º)*		
MC113	C_{46}-C_{45}-C_{26}-C_{27}	*-144.4*
MC114	C_{69}-C_{68}-C_{26}-C_{27}	*147.9*
MC115	C_{46}-C_{45}-C_{26}-C_{27}	*-166.8*
	S_{47}-C_{45}-C_{26}-C_{24}	*-166.7*
	S_{54}-C_{52}-C_{50}-S_{47}	*-179.7*
MC116	C_{46}-C_{44}-C_{68}-C_{24}	*147.9*
	N_{63}-C_{51}-C_{47}-C_{45}	*178.4*
	O_{69}-C_{47}-C_{45}-C_{44}	*177.7*
MC117	C_{45}-C_{44}-C_{69}-C_{26}	*145.6*
	S_{63}-C_{47}-C_{45}-C_{44}	*173.5*
	N_{64}-C_{51}-C_{49}-C_{46}	*-179.3*

Table S2. Experimental λ_{max},calculated excitation energies (eV), λ (nm) and oscillator strengths (f) and orbitals contribution to corresponding excited states, of **MC113-MC117** in DMF solvent, calculated at M06/LANL2DZ level

	λ_{exp} (nm)	λ_{cal} (nm)	State	f	Energy (eV)	Major contribution (%)*
MC113	632	816	S1	0.0554	1.51	H-1->LUMO (85%)
		657	S4	0.1274	1.88	HOMO->L+1 (89%)
		485	S8	0.1081	2.55	H-1->L+2 (36%), HOMO->L+3 (59%)
		479	S9	0.1149	2.58	H-1->L+3 (88%)
MC114	638	817	S1	0.0532	1.51	H-1->LUMO (85%)
		662	S4	0.1227	1.87	HOMO->L+1 (85%)
		536	S7	0.074	2.31	H-3->LUMO (95%)
		492	S9	0.2416	2.51	H-1->L+2 (25%), HOMO->L+3 (67%)
MC115	646	832	S1	0.0456	1.48	H-1->LUMO (87%)
		782	S3	0.0646	1.58	HOMO->LUMO (89%)
		666	S4	0.1072	1.86	HOMO->L+1 (89%)
		522	S7	0.5205	2.37	H-1->L+1 (19%), HOMO->L+2 (64%)
MC116	654	816	S1	0.0533	1.51	H-1->LUMO (85%)
		665	S4	0.1231	1.86	HOMO->L+1 (80%)
		580	S6	0.0505	2.13	H-2->LUMO (51%), H-1->L+1 (28%), HOMO->LUMO (16%)
		494	S10	0.2697	2.50	H-1->L+2 (23%), HOMO->L+3 (68%)
MC117	654	817	S1	0.0535	1.51	H-1->LUMO (85%)
		660	S4	0.1238	1.87	HOMO->L+1 (87%)
		519	S7	0.0533	2.38	H-3->LUMO (97%)
		489	S9	0.1833	2.53	H-1->L+2 (29%), HOMO->L+3 (64%)
	** The nature of all the calculated transitions mentioned above is of MLCT &LLCT type*					

Fig. S1. Chemical structures of the new sensitizers **MC113-MC117**, and **N749**.

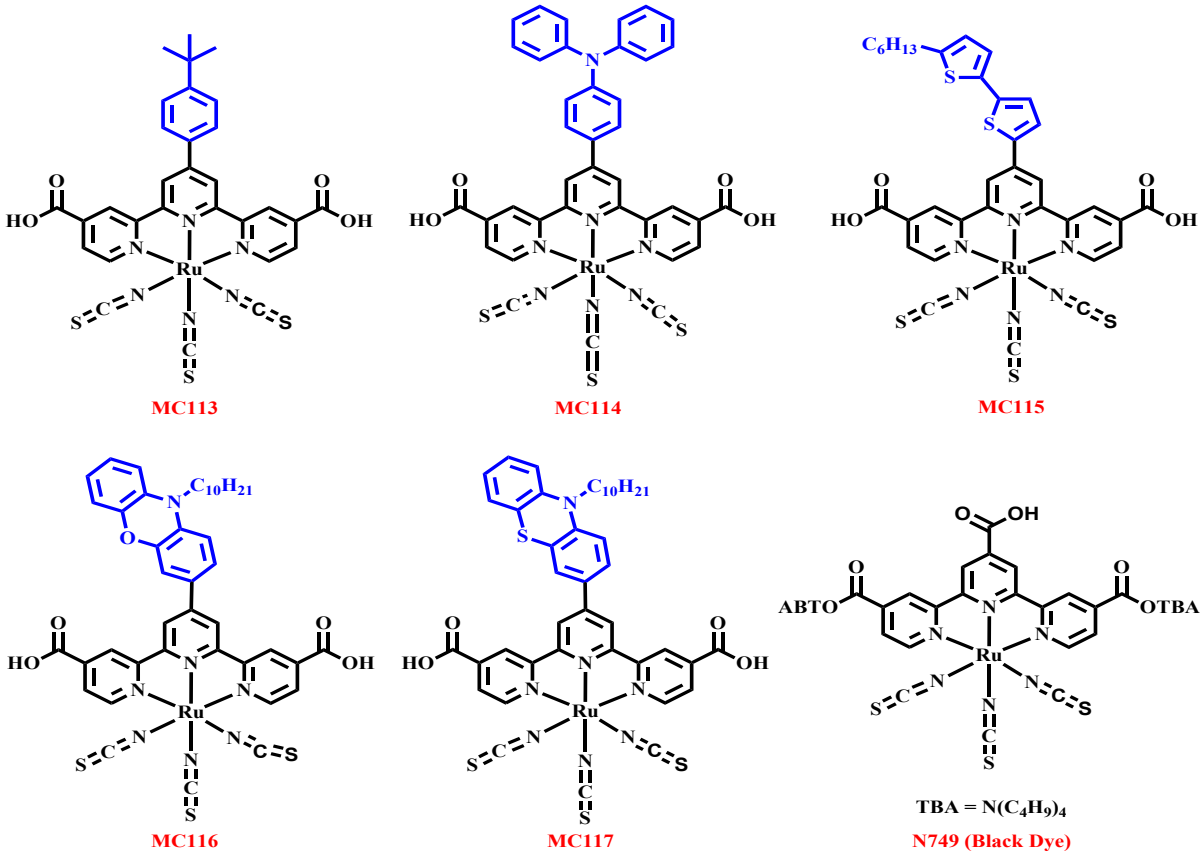
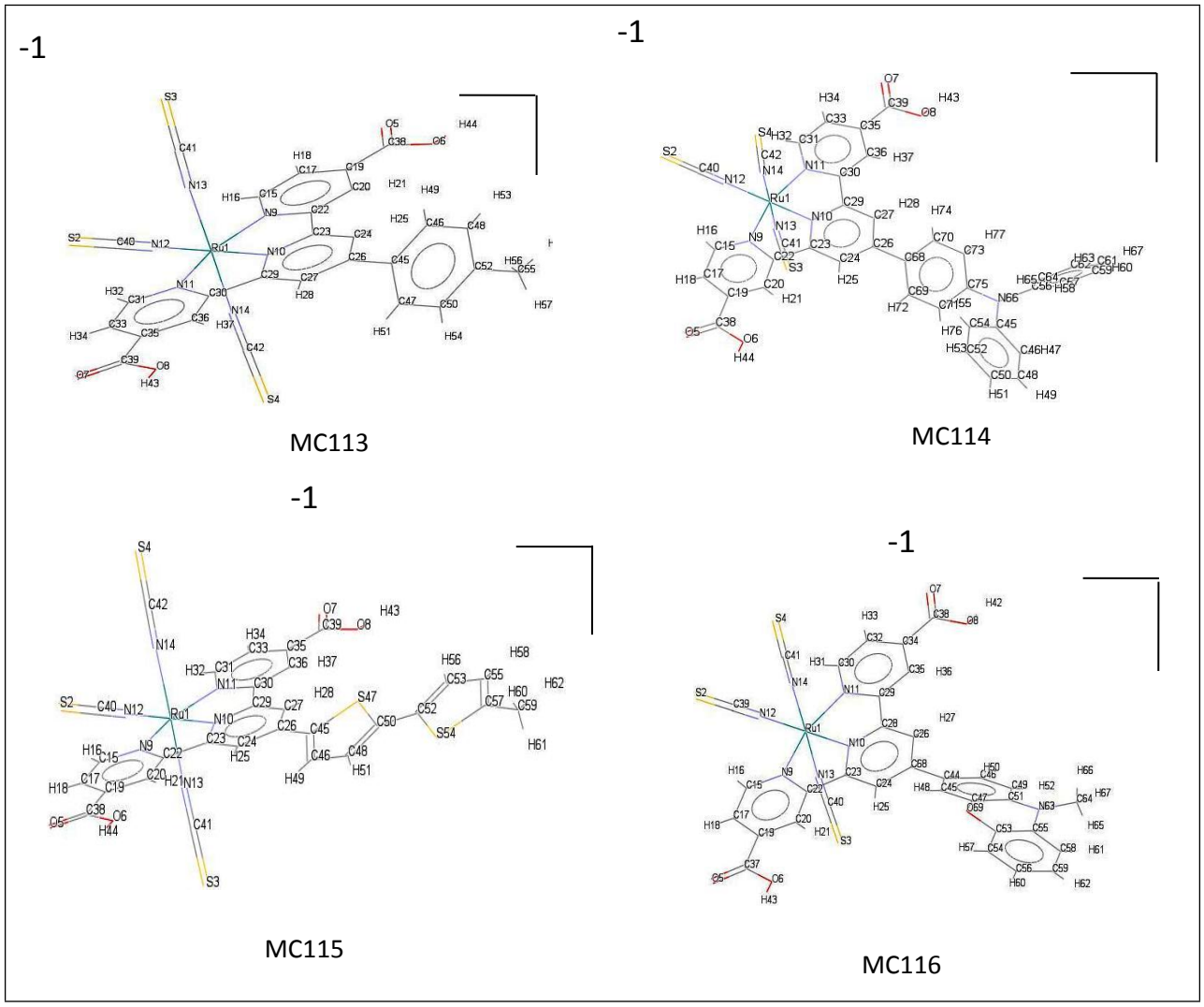
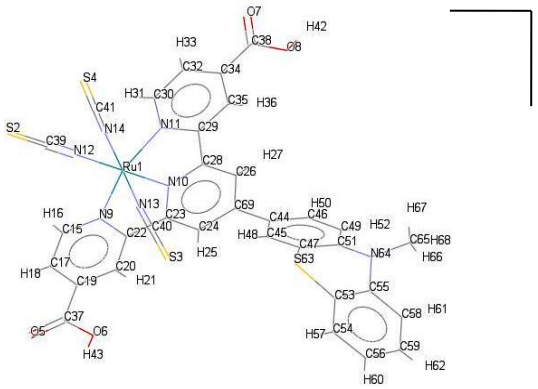


Fig. S2. Structures of optimized geometries of **MC113-MC117** at PBE0/ LANL2DZ level, in gas phase

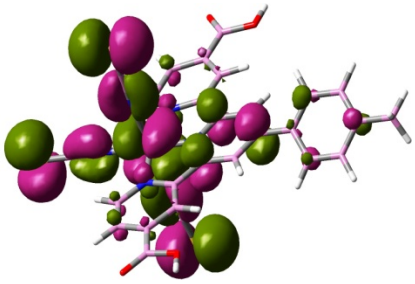
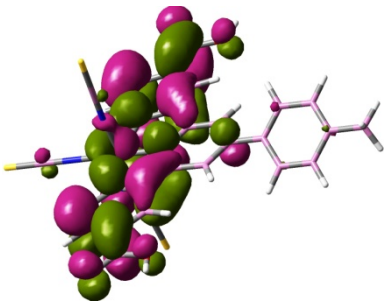
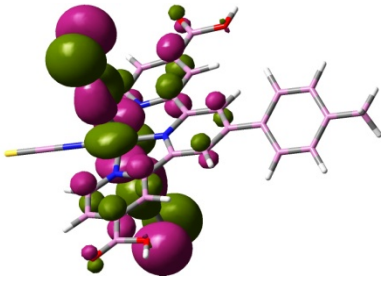
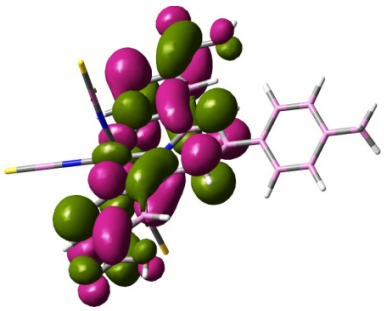


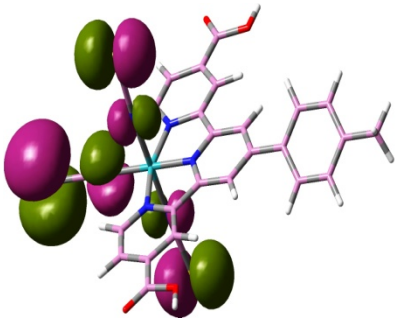
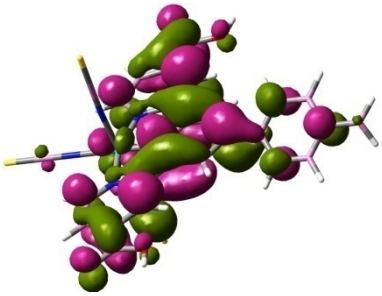
-1



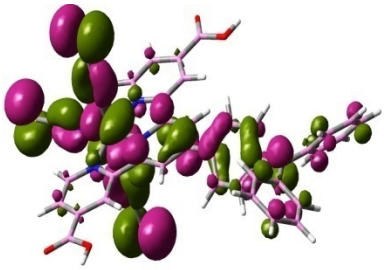
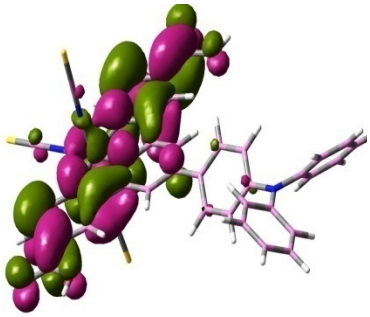
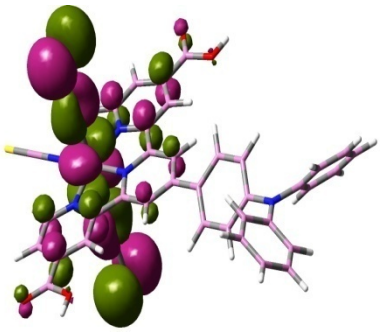
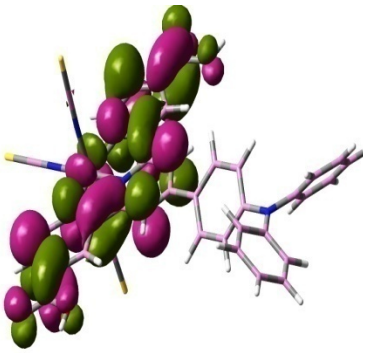
MC117

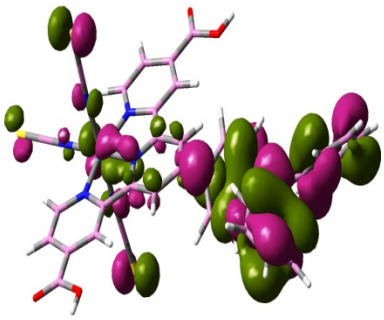
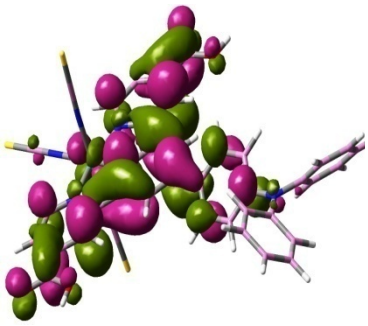
Fig. S3 (S3.a-S3.e). Isodensity plots of **MC113-MC117** (isovalue=0.02) in DMF, with percentagecontribution of groups to each molecular orbital, calculated at M06/LANL2DZ level.

TableS3.a	**MC113**
 HOMO	Ru (41%) NCS (43%) Terpyridine (14%) Chromophore(2%)
 LUMO	Ru (7%) NCS (2%) Terpyridine (90%) Chromophore(1%)
 HOMO-1	Ru (43%) NCS (45%) Terpyridine (12%) Chromophore(0%)
 LUMO+1	Ru (8%) NCS (1%) Terpyridine (91%) Chromophore(0%)

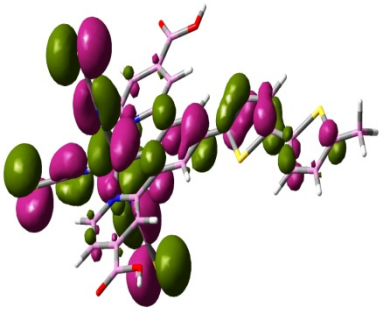
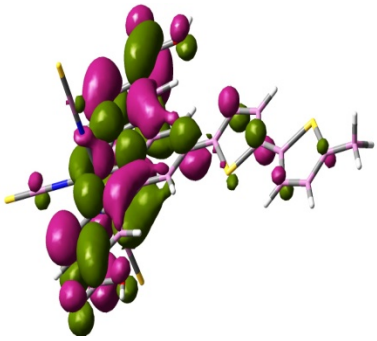
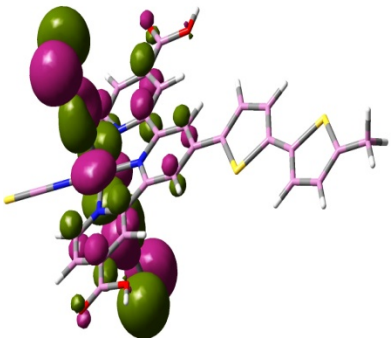
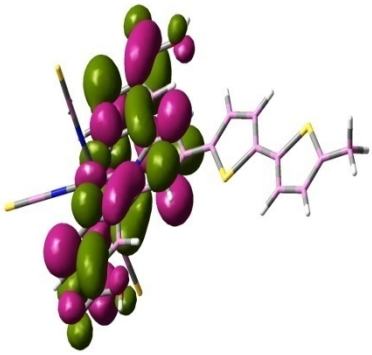
 HOMO-3	Ru (0%) NCS (100%) Terpyridine (0%) Chromophore(0%)
 LUMO+3	Ru (3%) NCS (1%) Terpyridine (88%) Chromophore(8%)

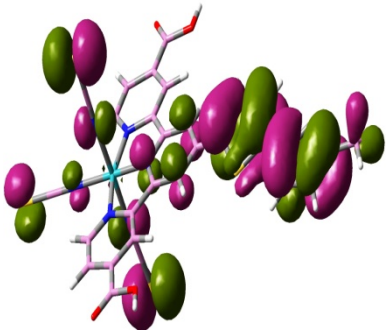
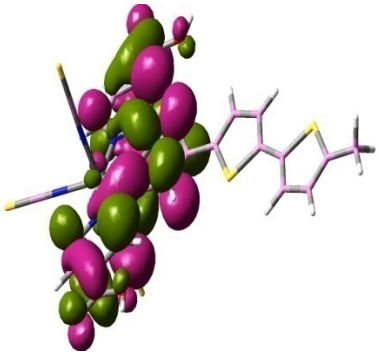
TableS3.b **MC114**

 HOMO	Ru (37%) NCS (37%) Terpyridine (12%) Chromophore (14%)
 LUMO	Ru (7%) NCS (2%) Terpyridine (89%) Chromophore (1%)
 HOMO-1	Ru (43%) NCS (45%) Terpyridine (12%) Chromophore (0%)
 LUMO+1	Ru (8%) NCS (1%) Terpyridine (91%) Chromophore (0%)

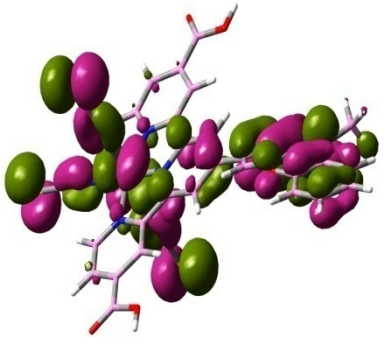
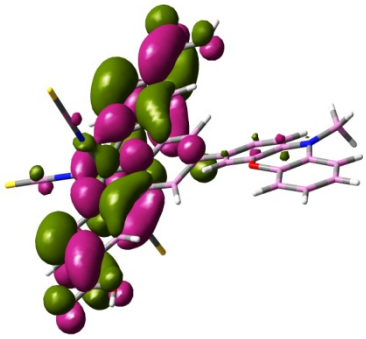
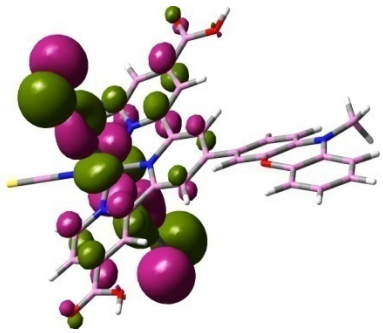
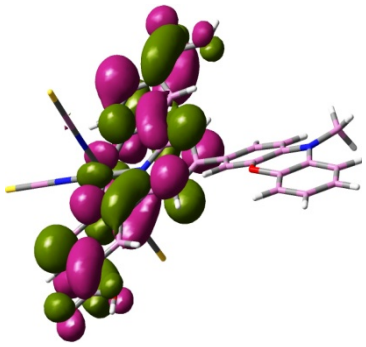
 Ru (4%) NCS (8%) Terpyridine (4%) Chromophore (84%) HOMO-3	 Ru (3%) NCS (1%) Terpyridine (84%) Chromophore (12%) LUMO+3

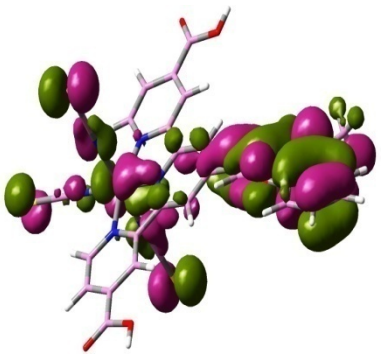
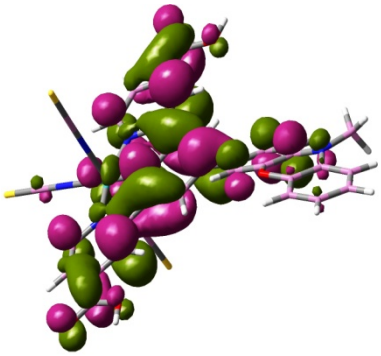
TableS3.c **MC115**

 Ru (39%) NCS (40%) Terpyridine (13%) Chromophore(9%) HOMO	 Ru (8%) NCS (3%) Terpyridine(84%) Chromophore (5%) LUMO
 Ru (43%) NCS (46%) Terpyridine(12%) Chromophore(0%) HOMO-1	 Ru (8%) NCS (1%) Terpyridine (91%) Chromophore (0%) LUMO+1

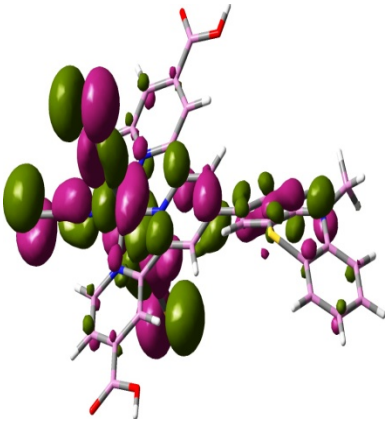
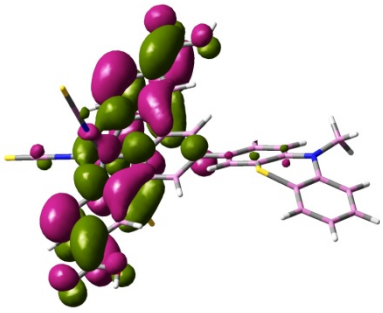
 HOMO-3 Ru (0%) NCS (28%) Terpyridine (7%) Chromophore(64%)	 LUMO+3 Ru (1%) NCS (0%) Terpyridine (99%) Chromophore (0%)

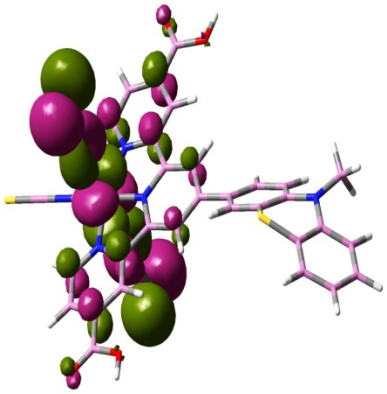
TableS3.d **MC116**

 HOMO Ru (32%) NCS (30%) Terpyridine (10%) Chromophore(28%)	 LUMO Ru (7%) NCS (2%) Terpyridine (90%) Chromophore(1%)
 HOMO-1 Ru (43%) NCS (45%) Terpyridine (12%) Chromophore(0%)	 LUMO+1 Ru (8%) NCS (1%) Terpyridine (91%) Chromophore(0%)

 Ru (9%) NCS (15%) Terpyridine (7%) Chromophore(69%) HOMO-2	 Ru (3%) NCS (1%) Terpyridine (85%) Chromophore(11%) LUMO+3

TableS3.e **MC117**

 Ru (39%) NCS (40%) Terpyridine (13%) Chromophore(9%) HOMO	 Ru (7%) NCS (2%) Terpyridine (90%) Chromophore(1%) LUMO



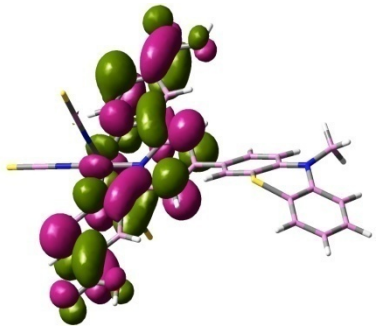
Ru (42%)

NCS (45%)

Terpyridine (12%)

Chromophore(0%)

HOMO-1



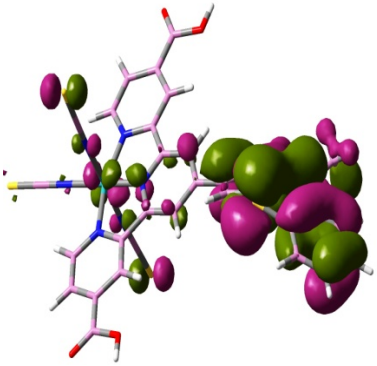
Ru (8%)

NCS (1%)

Terpyridine (91%)

Chromophore(2%)

LUMO+1



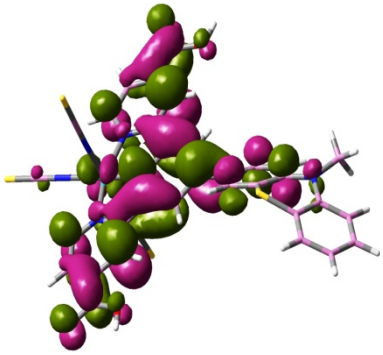
Ru (2%)

NCS (5%)

Terpyridine (3%)

Chromophore(89%)

HOMO-3



Ru (3%)

NCS (1%)

Terpyridine(85 %)

Chromophore(11%)

LUMO+3

Fig. S4. Normalized plots of simulated and experimental UV-Vis spectra of **MC113-MC117**. The green vertical bars correspond to the Oscillator strengths of calculated singlet excited states.