Electronic Supplementary Material (ESI) for RSC Advances
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4, 4'-Unsymmetrically substituted- 2, 2'-bipyridines: Novel bidentate ligands on ruthenium (II) [3+2+1] mixed ligand complexes for efficient sensitization of nanocrystalline TiO_2 in Dye Solar Cells.

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[2]Academy of Scientific and Innovative Research, CSIR-IICT

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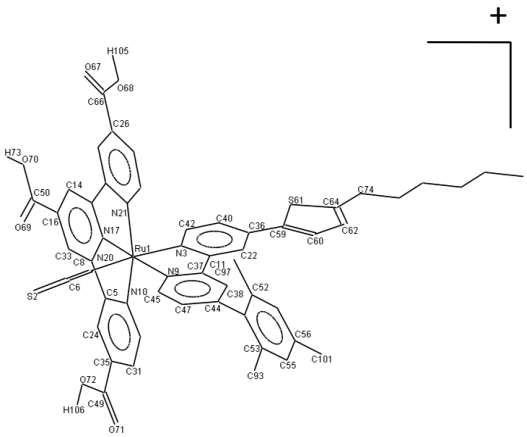
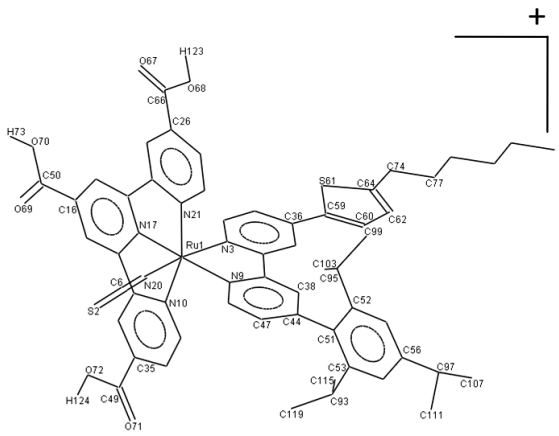
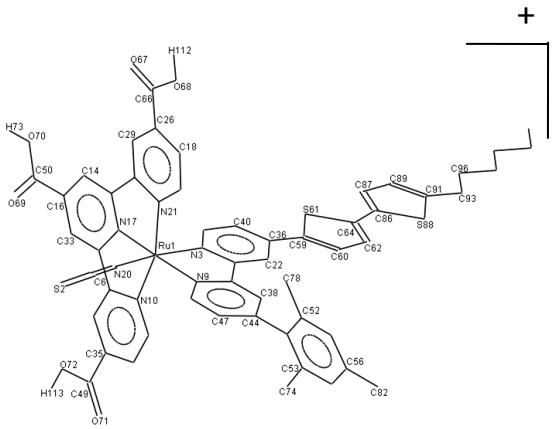
TableS1. Structures of optimized geometries of MC107-MC111 at B3LYP/ LANL2DZ level, in gas phase



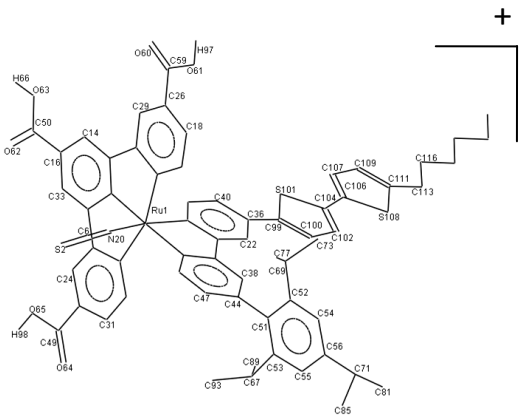
MC107



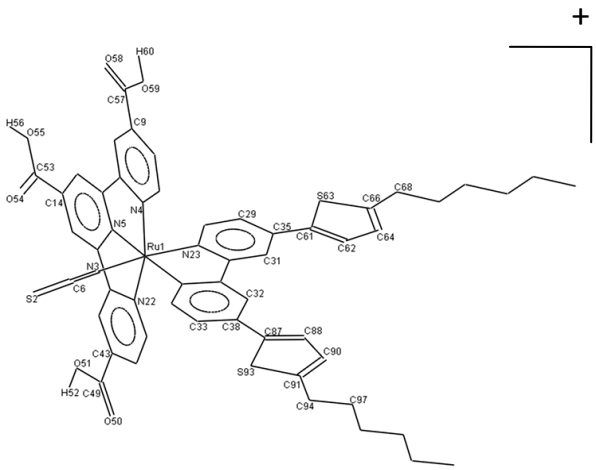
MC108



MC109



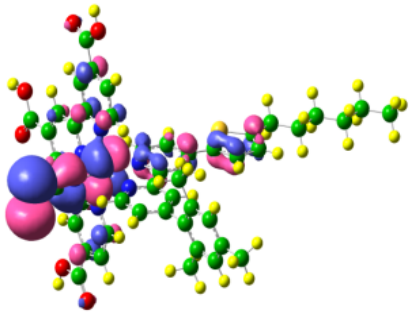
MC110



MC111

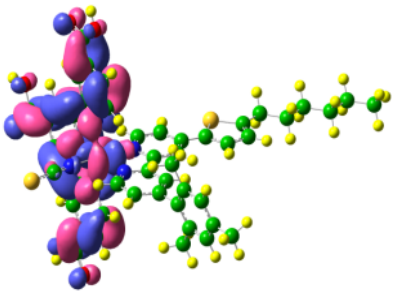
TableS2 (S2.a-S2.e). Molecular orbital pictures of MC107-MC111 (isovalue=0.02) in ethanol, with percentage contribution of groups to each molecular orbital, calculated at M06/LANL2DZ level

TableS2.a **MC107**



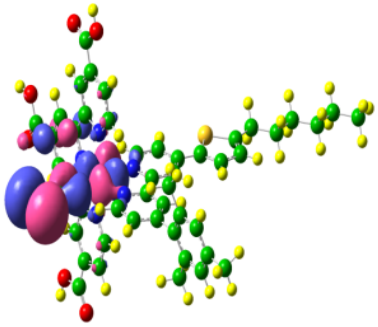
Ru (43%)
NCS (40%)
Bipy (9%)
Terpy (9%)

HOMO



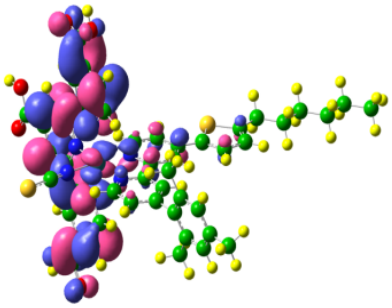
Ru (10%)
NCS (1%)
Bipy (1%)
Terpy (88%)

LUMO



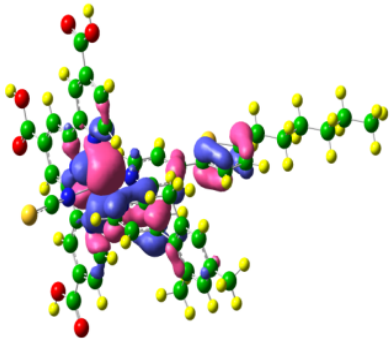
Ru (36%)
NCS (50%)
Bipy (1%)
Terpy (12%)

HOMO-1



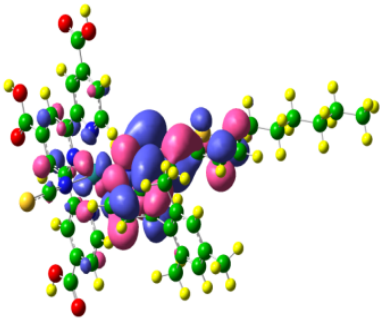
Ru (4%)
NCS (0%)
Bipy (8%)
Terpy (88%)

LUMO+1



Ru (71%)
NCS (1%)
Bipy (21%)
Terpy (8%)

HOMO-2



Ru (6%)
NCS (1%)
Bipy (86%)
Terpy (8%)

LUMO+2

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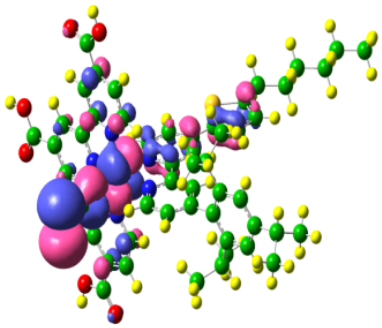
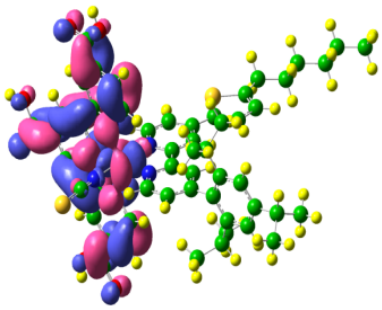
TableS2.b **MC108**



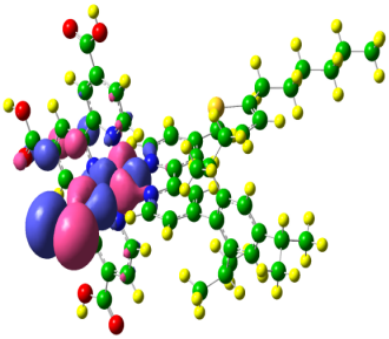
HOMO

Ru (43%)
NCS (40%)
Bipy (9%)
Terpy (9%)



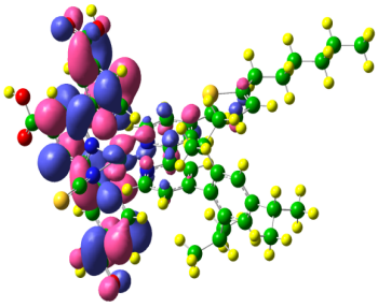
LUMO

Ru (10%)
NCS (1%)
Bipy (1%)
Terpy (88%)



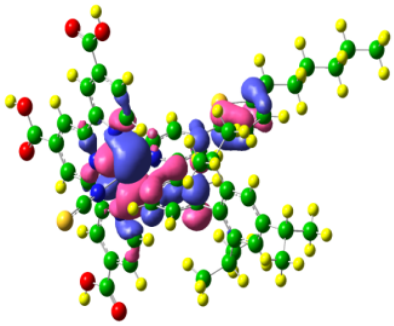
HOMO-1

Ru (36%)
NCS (51%)
Bipy (1%)
Terpy (12%)



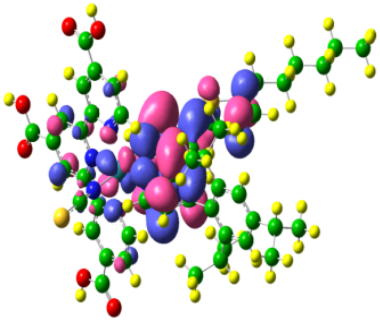
LUMO+1

Ru (4%)
NCS (0%)
Bipy (9%)
Terpy (88%)



HOMO-2

Ru (71%)
NCS (1%)
Bipy (20%)
Terpy (8%)



LUMO+2

Ru (6%)
NCS (1%)
Bipy (85%)
Terpy (8%)

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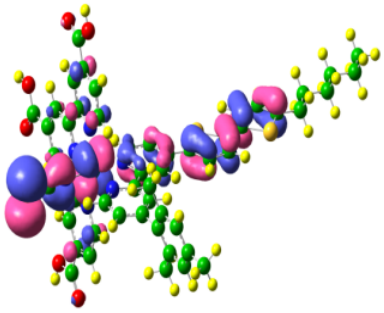
TableS2.c **MC109**



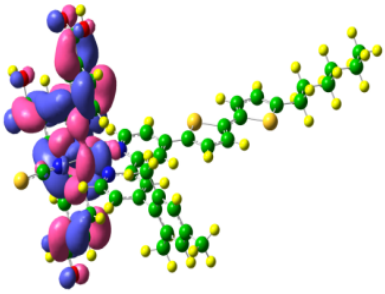
HOMO

Ru (37%)

NCS (31%)

Bipy (24%)

Terpy (7%)



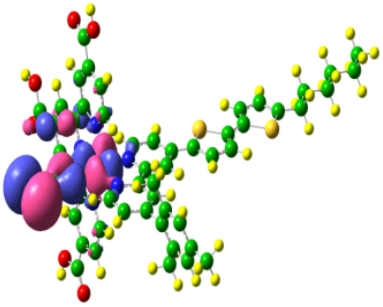
LUMO

Ru (10%)

NCS (1%)

Bipy (1%)

Terpy (88%)



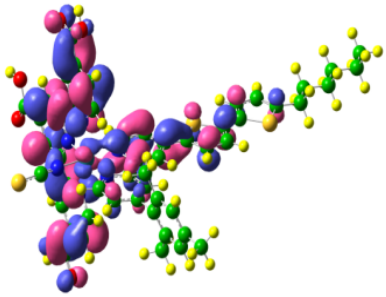
HOMO-1

Ru (36%)

NCS (51%)

Bipy (1%)

Terpy (12%)



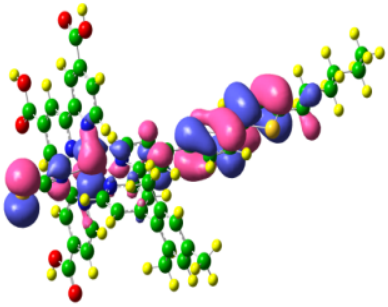
LUMO+1

Ru (2%)

NCS (0%)

Bipy (31%)

Terpy (67%)



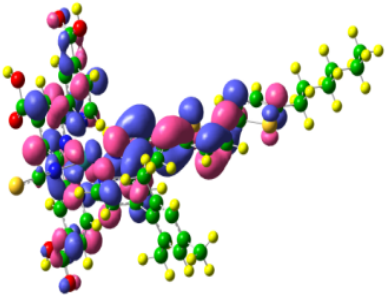
HOMO-2

Ru (18%)

NCS (13%)

Bipy (66%)

Terpy (3%)



LUMO+2

Ru (7%)

NCS (1%)

Bipy (65%)

Terpy (28%)

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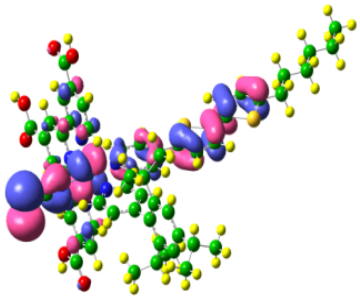
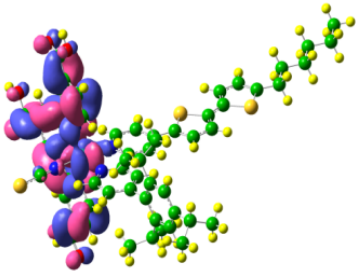
TableS2.d **MC110**



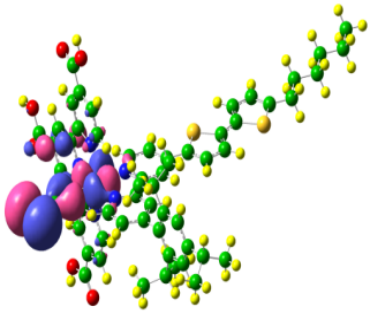
HOMO

Ru (37%)
NCS (32%)
Bipy (24%)
Terpy (7%)



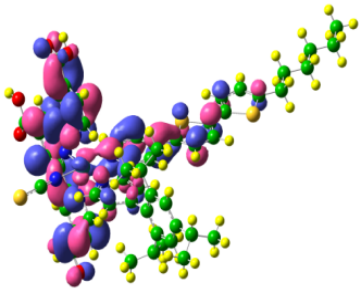
LUMO

Ru (10%)
NCS (1%)
Bipy (1%)
Terpy (88%)



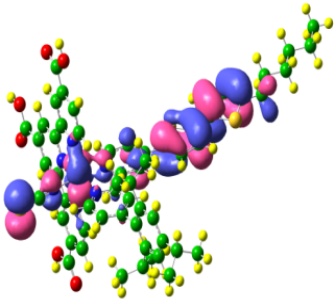
HOMO-1

Ru (36%)
NCS (51%)
Bipy (1%)
Terpy (12%)



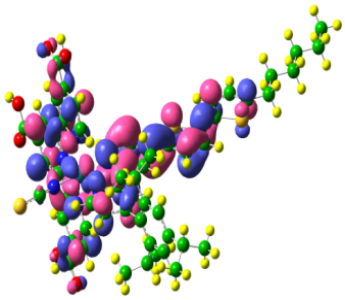
LUMO+1

Ru (2%)
NCS (0%)
Bipy (32%)
Terpy (66%)



HOMO-2

Ru (17%)
NCS (14%)
Bipy (67%)
Terpy (3%)



LUMO+2

Ru (7%)
NCS (1%)
Bipy (63%)
Terpy (29%)

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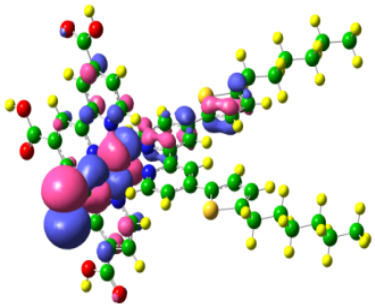
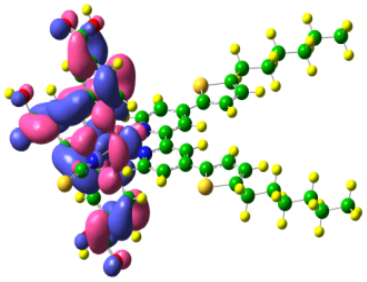
TableS2. e **MC111**



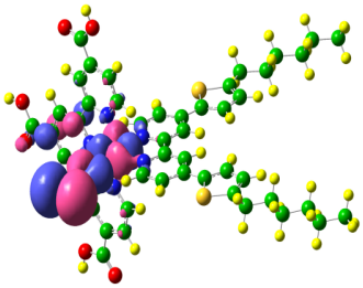
Ru (43%)
NCS (40%)
Bipy (9%)
Terpy (9%)

HOMO



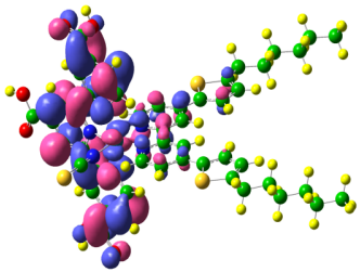
Ru (10%)
NCS (1%)
Bipy (1%)
Terpy (88%)

LUMO



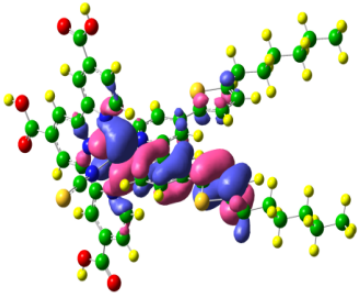
Ru (36%)
NCS (50%)
Bipy (1%)
Terpy (12%)

HOMO-1



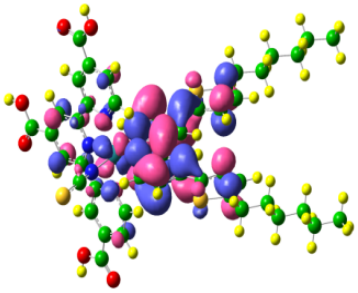
Ru (4%)
NCS (0%)
Bipy (11%)
Terpy (85%)

LUMO+1



Ru (58%)
NCS (0%)
Bipy (35%)
Terpy (6%)

HOMO-2



Ru (6%)
NCS (0%)
Bipy (83%)
Terpy (10%)

LUMO+2

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TableS3. Experimental λ_{max}, calculated excitation energies (eV), λ (nm) and oscillator strengths (f) of MC107-MC111 in ethanol solvent, calculated at M06/LANL2DZ level

	λ_{exp} (nm)	λ_{cal} (nm)	State	f	Energy (eV)	Major contribution (%) *
MC107	503	643	S3	0.0300	1.93	H-1->LUMO (78%), HOMO->L+1 (18%)
		550	S4	0.0917	2.26	HOMO->L+1 (63%)
		523	S6	0.0389	2.37	H-2->L+1 (23%) HOMO->L+2 (52%)
		500	S7	0.0106	2.48	H-2->L+1 (66%), HOMO->L+2 (22%)
MC108	507	643	S3	0.0303	1.93	H-1->LUMO (78%), HOMO->L+1 (17%)
		551	S4	0.0995	2.25	HOMO->L+1 (70%),
		524	S6	0.0363	2.37	H-2->L+1 (18%), HOMO->L+2 (54%)
MC109	509	643	S3	0.0290	1.93	H-1->LUMO (77%)
		563	S4	0.2567	2.20	HOMO->L+1 (78%)
		549	S5	0.0476	2.26	H-1->L+1 (74%), H-1->L+2 (20%)
		529	S6	0.0634	2.34	H-2->L+2 (15%), HOMO->L+2 (46%)
MC110	507	643	S3	0.0295	1.93	H-1->LUMO (78%), HOMO->L+1 (11%)
		564	S4	0.2551	2.19	HOMO->L+1 (78%)
		549	S5	0.0467	2.26	H-1->L+1 (73%), H-1->L+2 (21%)
		529	S6	0.0591	2.34	HOMO->L+2 (48%)
MC111	508	644	S3	0.0366	1.93	H-1->LUMO (78%), HOMO->L+1 (17%)
		553	S4	0.1060	2.24	HOMO->L+1 (69%), HOMO->L+2 (15%)
		535	S6	0.0303	2.3162	H-2->L+1 (26%), H-2->L+2 (16%), HOMO->L+2 (42%)
		513	S7	0.0305	2.4161	H-2->L+1 (61%), HOMO->L+2 (26%)

* *The nature of all the calculated transitions mentioned above is of MLCT&LLCT type*

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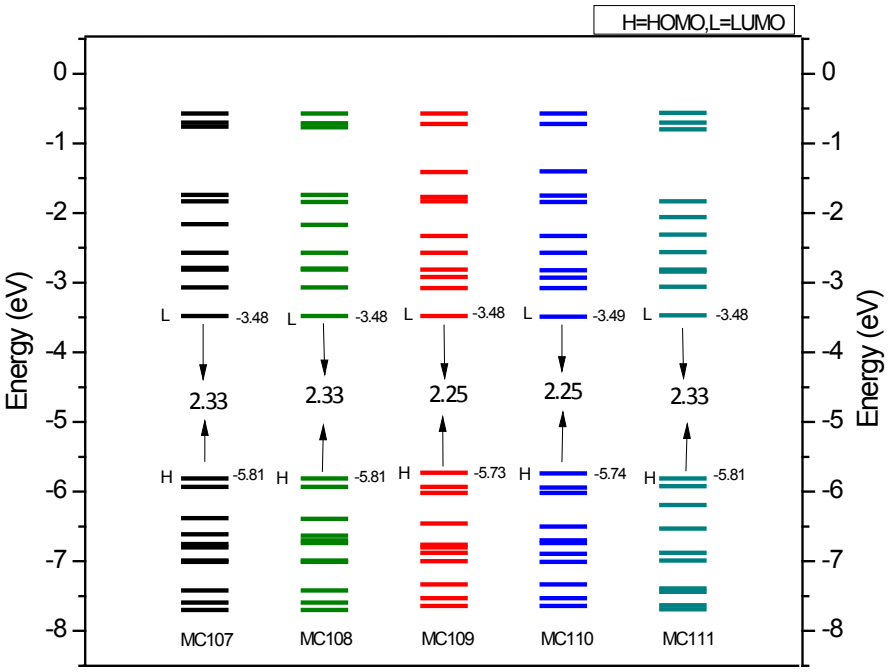
FigS1. Calculated HOMO-LUMO energies and HOMO-LUMO gaps of MC107-MC111, calculated at B3LYP/LANL2DZ level of theory in ethanol solvent