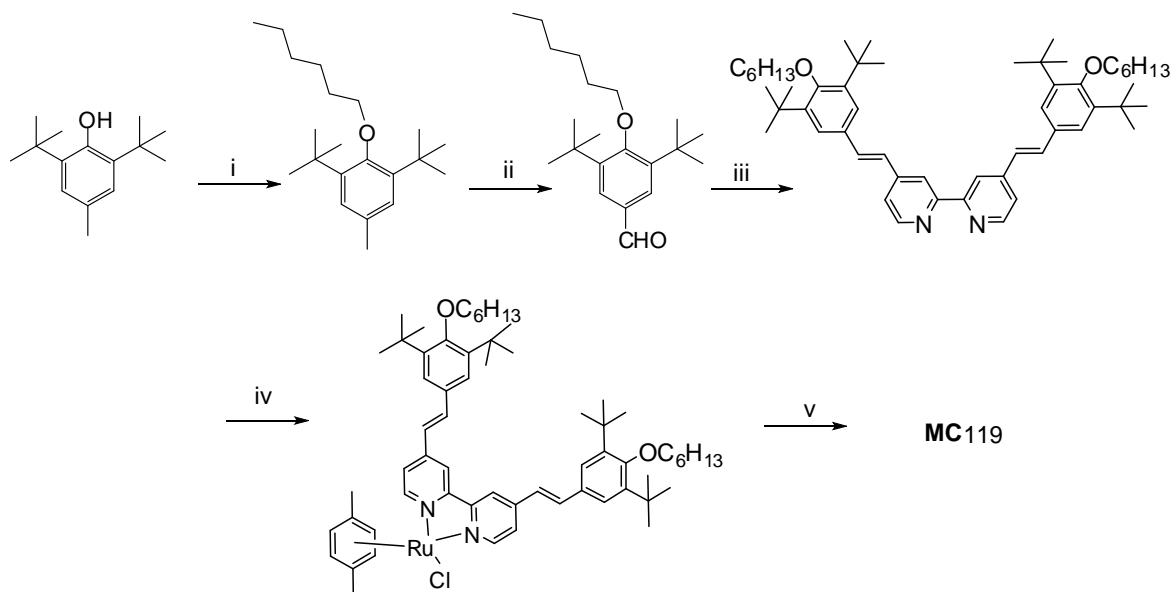


Functionalized Styryl Bipyridine as superior Chelate on Ruthenium Sensitizer for Dye Sensitized Solar Cells.

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The synthesis of ruthenium complexes **MC119** is carried out according to scheme 1. Commercially available 2, 5-di-*tert*-butyl-4-methyl phenol was subjected to alkylation using hexyl bromide and KOH in DMF solvent at room temperature to obtain the *o*-alkylated product in 80% yield. The alkylated product underwent oxidation at methyl position to afford the 3,5- di *tert* butyl-4-hexyloxy benzaldehyde in good yield. The aldehyde is then subjected to condensation with bipyridine diphosphonate under wittig reaction conditions to obtain the ancillary ligand. All the new compounds and the ruthenium complex **MC119** are fully characterized with IR, ¹HNMR and Mass spectra.



Reagents and conditions: i) $C_6H_{13}Br$, KOH, DMF, RT, 12h; ii) (a) NBS, AIBN, 24h, (b) $CaCO_3$, H_2O , 24h; iii) 2,2'-bipyridine-4,4'-diphosphonate, NaH, THF, reflux, 12h; iv) Ru-p-cymene complex, DMF, 60-70°C, 4 h, v) 2,2'-bipyridine-4,4'-dicarboxylic acid, NH_4NCS , DMF, reflux, 8 h.

Scheme 1: Synthesis scheme for the sensitizer **MC119**

Synthesis of 1, 3-di-tert-butyl-2-(hexyloxy)-5-methylbenzene (1):

To a stirring suspension of potassium hydroxide (2.83g, 50.545mmol) in dimethylformamide (40 mL) at ambient temperature under nitrogen atmosphere was added 2, 6-di-tert-butyl-4-methylphenol (4.0g, 18.18mmol). After stirring vigorously for 30 min, 1-bromohexane (5.071mL, 36.36mmol) was added and the stirring was continued for 12 h at the same temperature. After complete consumption crushed ice was added and stirred for 30 minutes then extracted with ethyl acetate. Concentrated to dry on Rota evaporator and purified by column chromatography (silicagel) using hexane as eluent (4.421 g, 80%). ¹H NMR (CDCl₃, 25⁰C, 500MHz) δ: 0.90 (t, 3H), 1.34 (m, 6H), 1.38 (s, 18H), 1.82 (q, 2H), 2.25 (s, 3H), 3.64 (t, 2H), 6.94 (s, 2H). Chemical formula C₂₁H₃₆O: ESI-MS: Calcd for (M+H)⁺: 305, found: 305 (50%).

Synthesis of 3, 5-di-tert-butyl-4-(hexyloxy)benzaldehyde (2):

To a solution of 10.00 g (1.5g, 4.93mmol) of **1** in 200 mL of CCl₄, 9.74g (0.966g, 5.421 mmol) of *N*-bromosuccinimide (NBS) and a catalytic amount of α-α'-azobisisobutyronitrile (AIBN) were added. The reaction was refluxed for 12 h. Then, the same amount of NBS and AIBN were added and refluxed again. The mixture was cooled, filtered, and concentrated. The crude product was purified by column chromatography. This product was refluxed for 24 h with a mixture of 21.45 g (214.3 mmol) of CaCO₃ in 100 mL of water. Following cooling, the mixture was extracted with EtOAc (2x100 mL) and the organic layer was washed with saturated NH₄Cl (40 mL), dried with MgSO₄, filtered and concentrated. Purification by column chromatography (hexane/EtOAc 9:1) (0.229 g, 65%). ¹H NMR (CDCl₃, 25⁰C, 300MHz) δ: 0.91 (t, 3H), 1.35 (m, 6H), 1.44 (s, 18H), 1.90 (q, 2H), 3.70 (t, 2H), 7.72 (s, 2H), 9.86 (s, 1H). Chemical formula C₂₁H₃₄O₂: ESI-MS: Calcd for (M+H)⁺: 319, found: 319 (100%).

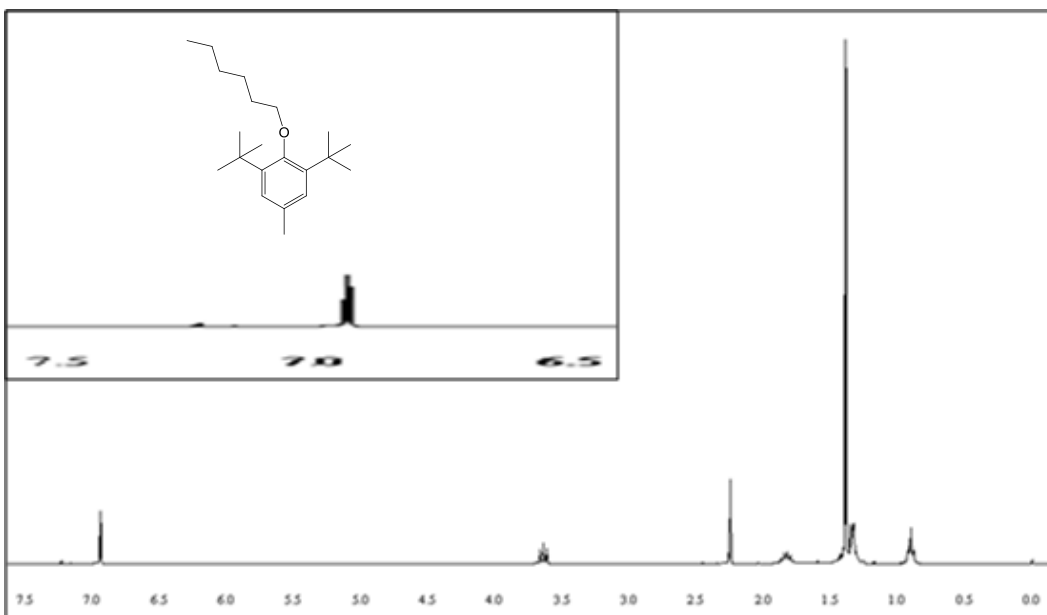
Synthesis of 4, 4'-bis((E)-3,5-di-tert-butyl-4-(hexyloxy)styryl)-2,2'-bipyridine (3):

Sodium hydride (0.126 g, 5.261mmol) was washed (3 times) with dry hexane and THF (5 ml) was added. To this suspension, a THF solution of bipyridine diphosponate (400 g, 0.877mmol) was added and the resulting mixture was stirred at room temperature for 30 minutes. Then **2** (0.669 g, 2.105mmol) dissolved in THF was added drop-wise at room temperature while stirring. The reaction mixture was refluxed for 12 h. After cooling to room temperature, the mixture was filtered through a short plug of silica gel using diethyl ether or dichloromethane. The filtrate was concentrated and methanol was added. The product was precipitated, filtered and washed with cool methanol. The solid was dried to obtain the product (0.585 g, 85%). ¹H NMR (CDCl₃, 25⁰C, 300MHz) δ: 0.89 (t, 3H), 1.31 (m, 6H), 1.62 (q, 6H), 2.62 (t, 2H), 6.92 (d, 1H), 6.95 (d, 1H), 7.24 (dd, 1H). Chemical formula C₅₄H₇₆N₂O₂: ESI-MS: Calcd for (M+H)⁺: 786, found: 786 (95%).

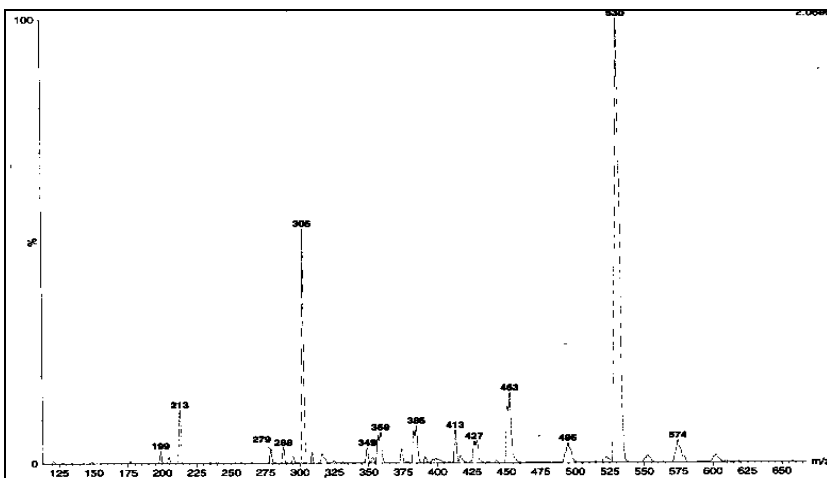
Synthesis of MC119 Dye:

Compound **3** (0.100 g, 0.127 mmol) and dichloro(*p*-cymene)ruthenium(II) dimer (0.039 g, 0.063 mmol) in dry DMF were heated at 60⁰C for a period of 4 hours under argon in the dark. Subsequently 4,4''-dicarboxylic acid-2,2''-bipyridine (0.031 g, 0.127 mmol) was

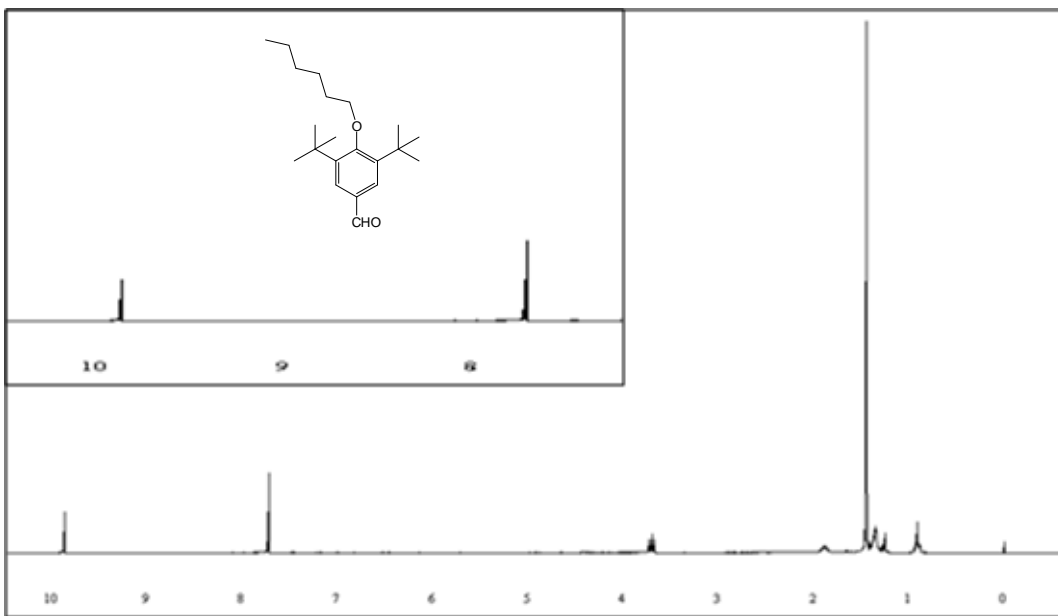
added and the reaction mixture was heated to 140⁰C for another 4 hours. To the resulting dark green solution was added NH₄NCS (0.290 g, 3.821 mmol) in water (2 ml) and the reaction mixture was further heated for 3 hours at 150⁰C. DMF was removed on rotaevaporator under high vacuum and water (250 ml) was added to get the precipitate. The solid was filtered off, washed with water and diethyl ether, and dried under vacuum. The crude compound was dissolved in methanol and dichloromethane and further purified on the sephadex LH-20 with methanol/ dichloromethane (60/ 40 v/v) as eluent about three times to get pure **MC119** as dark brown solid (0.090 g, 60%). ¹H NMR (CDCl₃, 25⁰C, 300MHz) δ: 0.77 (t, 6H), 1.22 (m, 12H), 1.32 (s, 18H), 1.40 (s, 18H), 1.76 (q, 4H), 3.60 (tt, 4H), 6.77 (d, 1H) ,6.95-7.05 (m, 4H), 7.32-7.62 (m, 9H), 8.07 (s, 1H), 8.21 (s, 1H), 8.64 (s, 1H), 8.77 (s, 1H), 9.18 (d, 1H), 9.48 (d, 1H). Chemical formula C₆₈H₈₄N₆O₆RuS₂; ESI-MS: Calcd for (M+H)⁺: 1247, found:1247 (70%). IR (KBr): ν = 2922cm⁻¹(CH₃), 2192(acetylene), 2097(NCS), 1603(COO⁻_{asym}), 1523(BPy), 1466(BPy), 1306(COO⁻_{sym}).



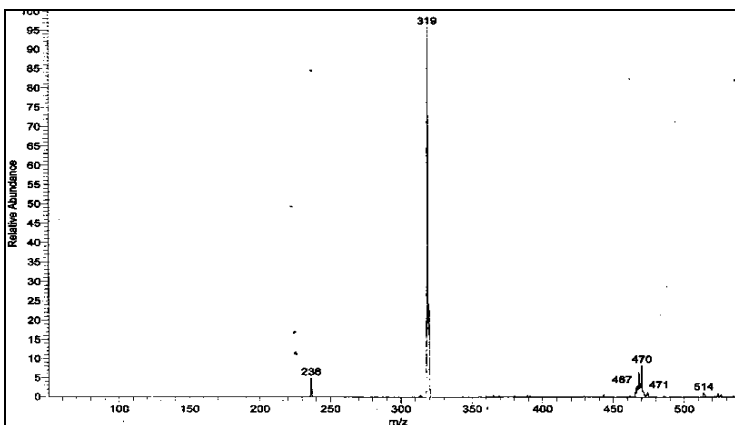
¹H NMR spectrum of 1,3-di-tert-butyl-2-(hexyloxy)-5-methylbenzene



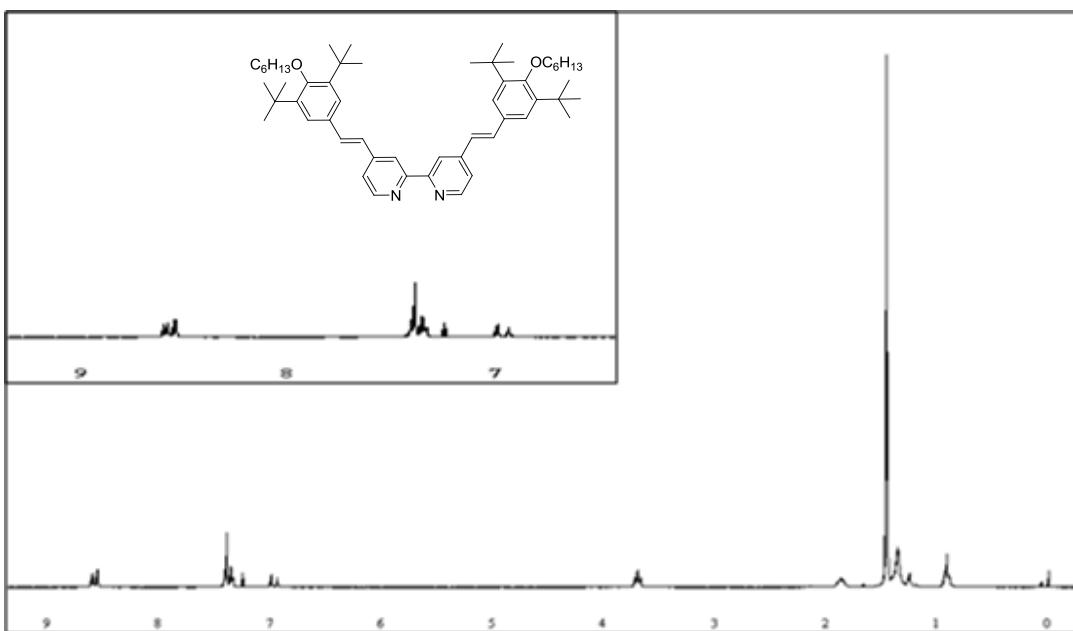
ESI-MS spectrum of 1, 3-di-tert-butyl-2-(hexyloxy)-5-methylbenzene



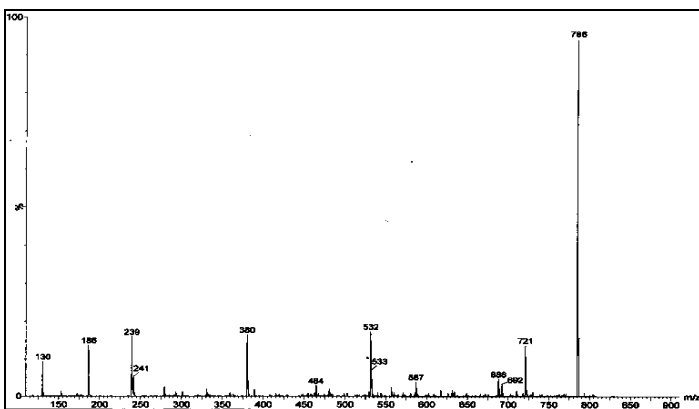
¹H NMR spectrum of 3, 5-di-tert-butyl-4-(hexyloxy) benzaldehyde



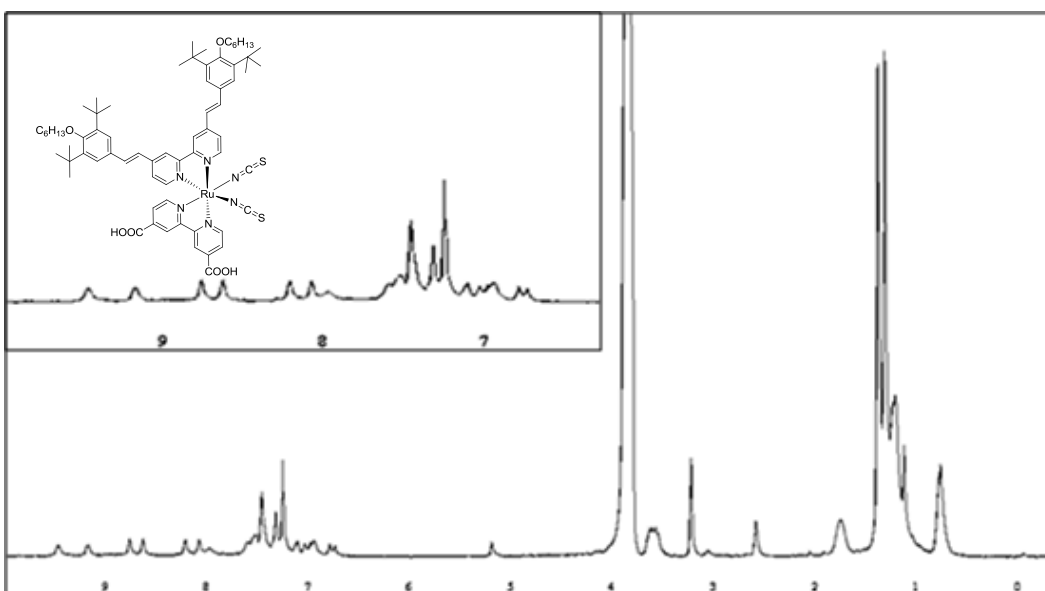
ESI-MS spectrum of 3,5-di-tert-butyl-4-(hexyloxy) benzaldehyde



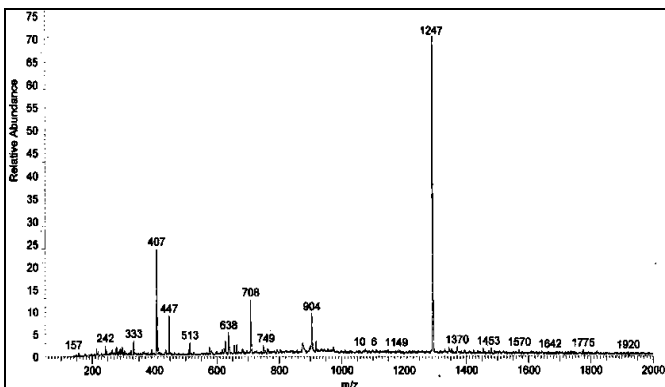
¹H NMR spectrum of **MC119** ligand



ESI-MS spectrum of MC119 ligand



¹H NMR spectrum of MC119



ESI-MS spectrum of MC119

Computational details: Gaussian 09 was employed for all the calculations. The ground state geometry of complex MC119 was optimized by hybrid functional Becke Three Parameter B3LYP with Los Alamos electron effective core potential LANL2DZ basis set was selected for our study.

In order to reduce the computational cost we have replaced the O-hexyl group of the ancillary Ligand(L_A) with a methoxy group, as alkyl chain hardly have any influence in spectral properties. The methoxy groups position with respect to the molecular plane also hardly effects the spectroscopic data hence the two methoxy groups were taken *trans* to each other (figure 1). The optimized geometry was confirmed to be potential energy minima by vibrational frequency calculation at the same level of theory as no imaginary frequencies were found. In the calculation the quasi-relativistic pseudo-potentials proposed by Hay and Wadt and a double zeta quality basis set LANL2DZ was adopted on all the atoms.

At the optimized geometry TDDFT calculations were performed at same level of theory in DMF by means of PCM solvation model as implemented in the Gaussian 09 program package. 70 singlet-singlet excitations at the S_0 optimized geometry allowed us to simulate a large (upto 300 nm) portion of the absorption spectrum and gain insight into the nature of the transitions giving rise to the low energy spectral region.

Molecular geometry structure in ground state: The optimized complex MC119 in the ground state is shown in fig: 1

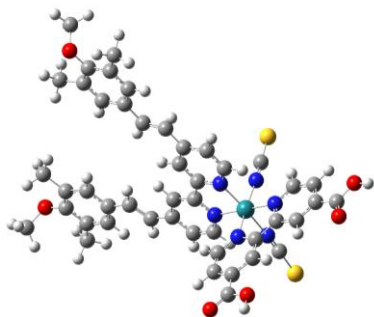
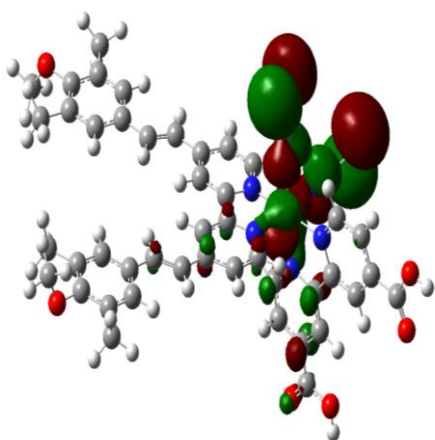


Fig:1 Optimised geometry of MC119.

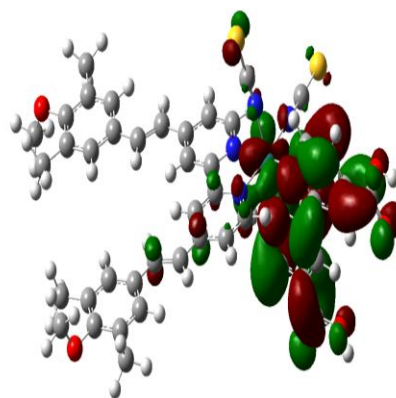
To gain insight into the electronic structure of complex MC119 we report in table 1 the important molecular orbital composition and in figure 2 the isodensity surface plots of some selected molecular orbitals. The calculations show that HOMO(H) is centered on Ru-d orbitals and the NCS ligand whereas the LUMO(L) is a π^* orbital centered mainly on the cyclometalating ligand(dcbpy). H - 1, H - 2 are localized on NCS ligand and whereas L+1 is localized mainly on the ancillary Ligand(L_A) and also on dcbpy. L+2 is delocalized on dcbpy and a part of L_A . In short the major contribution for highest occupied orbitals are composed of NCS ligand and Ru(d) orbitals. For the lowest unoccupied have both dcbpy and L_A compositions.

Table 1. Molecular orbital composition(%) in the ground state at the B3LYP/LANL2DZ level for MC119

Orbital Nature	Energy(eV)	Ru	Ru(d)	NCS	dc bpy	L _A	Main bond
HOMO-5	-6.153	42.7	42.4	17.1	6.2	34.0	Ru(d)+ L _A
HOMO-4	-6.108	37.7	37.5	7.6	6.3	48.4	L _A +Ru(d)
HOMO-3	-4.913	0.4	0.3	97.0	1.4	1.2	NCS
HOMO-2	-4.834	14.2	14.1	76.9	5.3	3.6	NCS
HOMO-1	-4.798	13.2	13.0	78.8	4.8	3.2	NCS
HOMO	-4.651	20.9	20.6	66.9	7.9	4.4	NCS + Ru(d)
LUMO	-3.185	9.7	9.7	2.4	81.2	6.7	dc bpy
LUMO+1	-2.881	5.2	5.1	1.1	16.9	76.9	L _A +dc bpy
LUMO+2	-2.730	4.7	4.7	0.7	82.9	11.7	dc bpy
LUMO+3	-2.557	2.0	1.9	0.2	2.6	95.2	L _A
LUMO+4	-2.351	0.3	0.1	0.1	42.8	56.8	L _A +dc bpy
LUMO+5	-2.222	0.5	0.1	0.4	56.3	42.8	dc bpy+ L _A



HOMO



LUMO

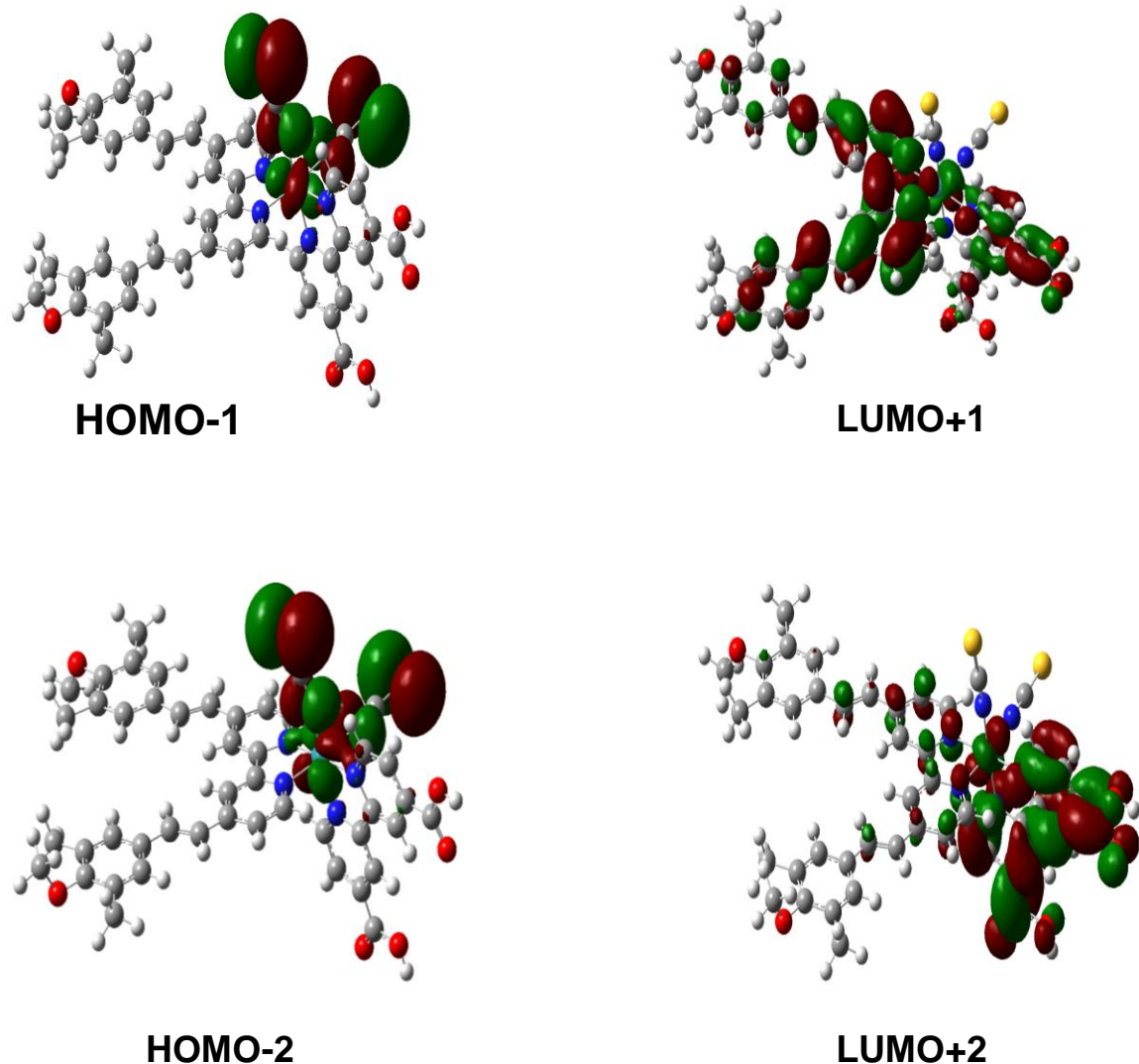


Fig 2. Isodensity surface plots of frontier orbitals of MC119 obtained from DFT calculations .

TD-DFT calculations:

TDDFT calculations were employed to understand better the nature of the excited states and examine the vertical excitation energies. TDDFT calculations in the framework of the PCM model in DMF solvent gives very good agreement with experimental one. Figure 3 shows the simulated spectra,

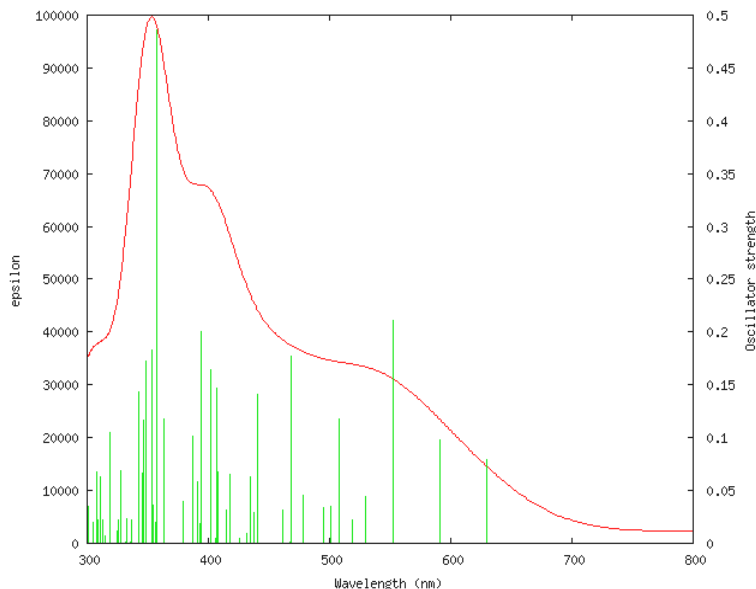


Fig 3. Simulated UV-Vis absorption spectra for MC119 at B3LYP/LANL2DZ level in solvent (DMF) phase

Calculated first 10 singlet excited states along with their energies and oscillatory strength are given in table 2.

The λ_{\max} peak is mainly from homo energy level to L+1 and L+2 indicating that the transition is a mixture of LLCT and MLCT.

Table 2. Singlet excited states calculated at the B3LYP/LANL2DZ level using PCM solvation model for MC119

States	Participating MO	E(eV)	λ (nm)	f
S1	HOMO->LUMO (88%)	1.5390	805.62	0.0283
S2	H-1->LUMO (94%)	1.7353	714.48	0.0004
S3	H-2->LUMO (72%)	1.9688	629.75	0.0787
S4	HOMO->L+1 (58%)	2.0958	591.58	0.0983
S5	HOMO->L+2 (35%) HOMO->L+1 (-29%)	2.2457	552.09	0.2112
S6	H-1->L+1 (89%)	2.3410	529.62	0.0444
S7	H-2->L+1 (41%)	2.3907	518.62	0.0218
S8	H-2->L+2 (38%) H-1->L+2 (37%)	2.4387	508.39	0.1173
S9	H-2->L+1 (46%)	2.4726	501.43	0.0349
S10	H-3->LUMO (75%)	2.5061	494.74	0.0335