Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Engineering of cis-Ru(II) dyes based on dissymmetric bipyridine ligands for interfacial and light-harvesting optimization

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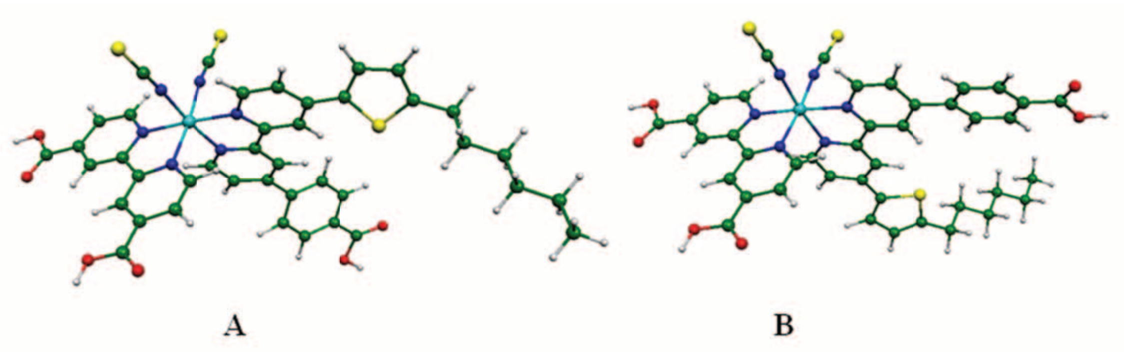


Figure S1. Optimized molecular structure of the **MC112** isomers **A** and **B**.

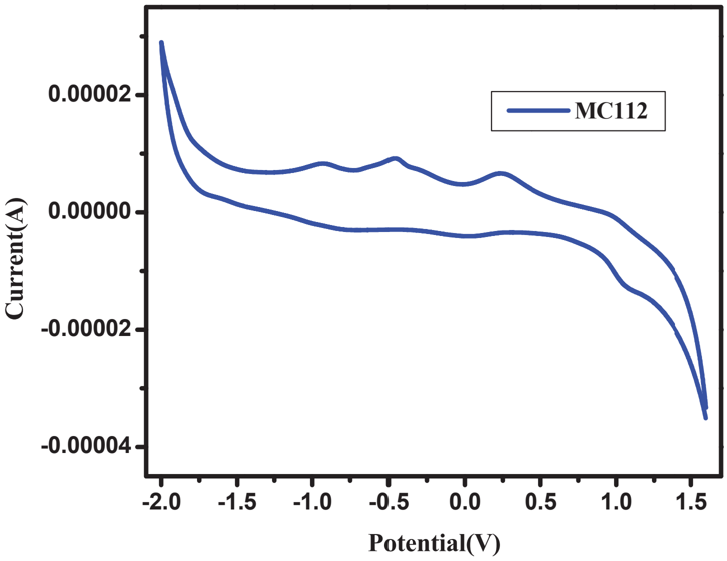


Figure S2. Cyclic voltammogram of MC112 dye.

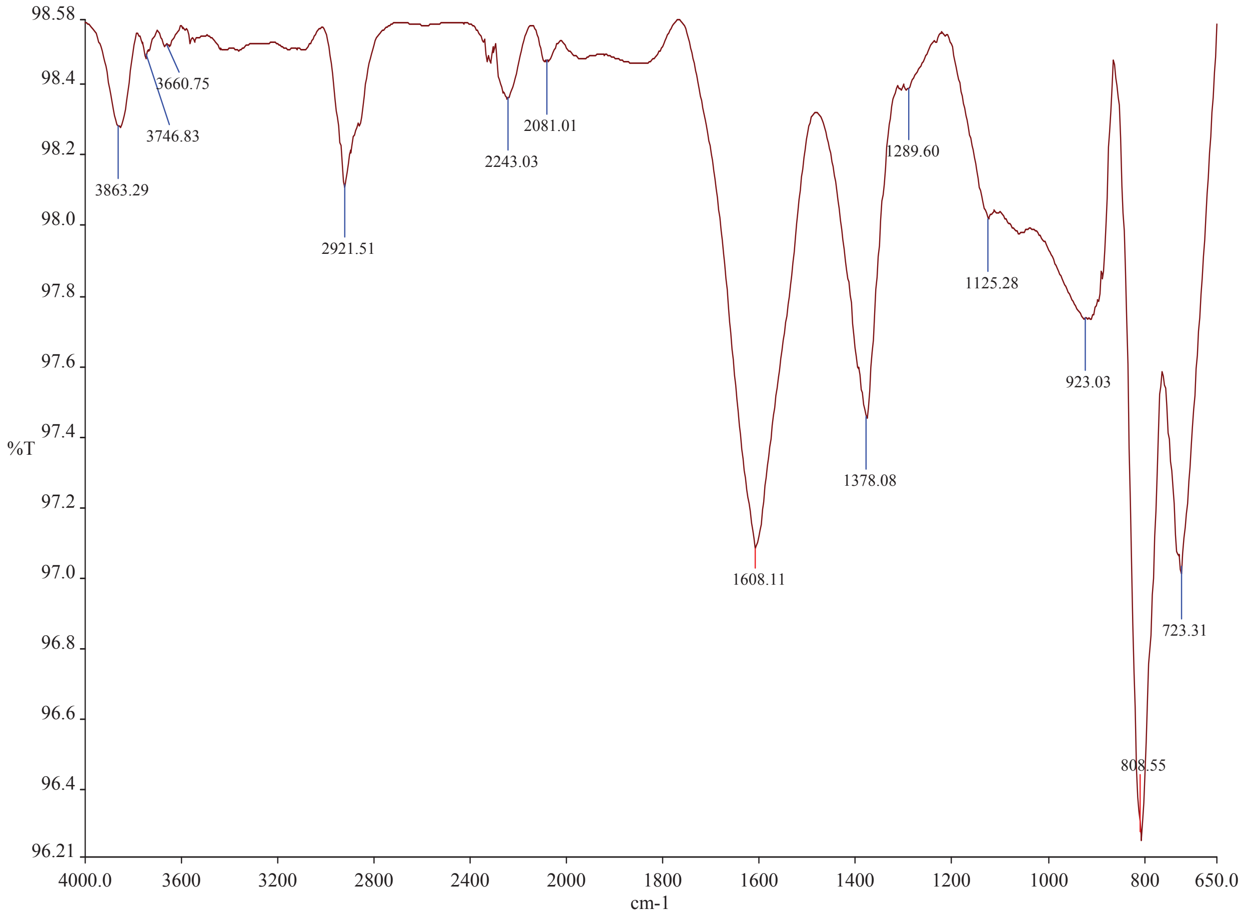


Figure S3. FT-IR spectrum of the MC112 dye adsorbed on TiO_2.

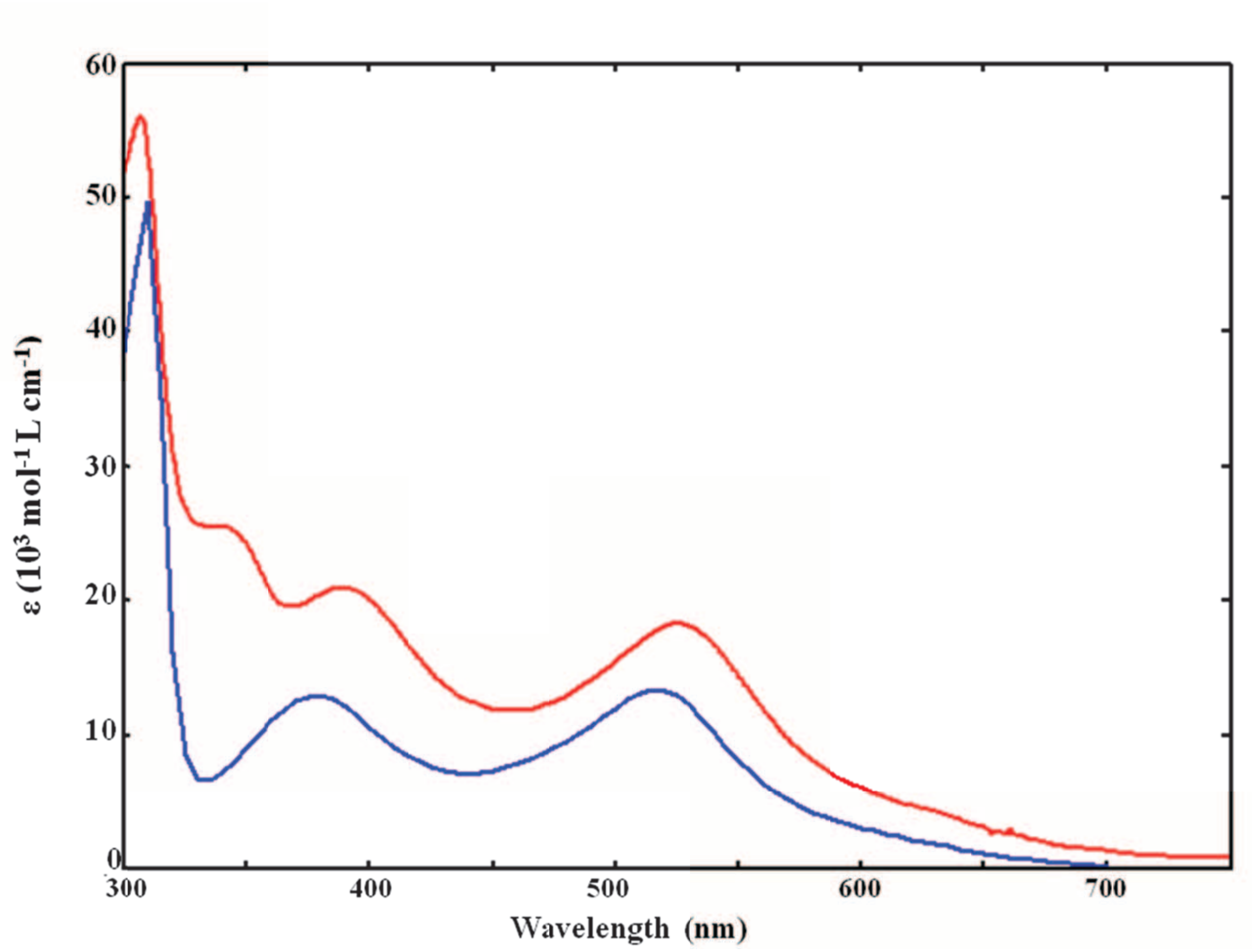


Figure S4. Comparison between experimental absorption spectra of MC112 (blue lines) and monoprotonated N3[1] (red lines).

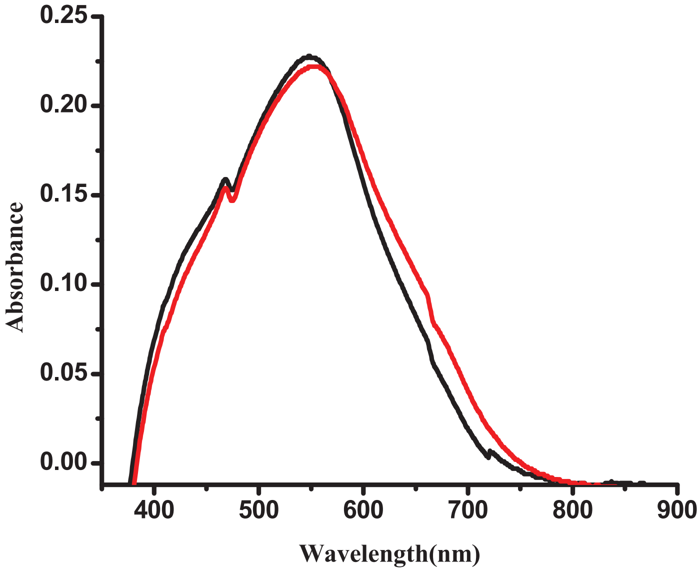
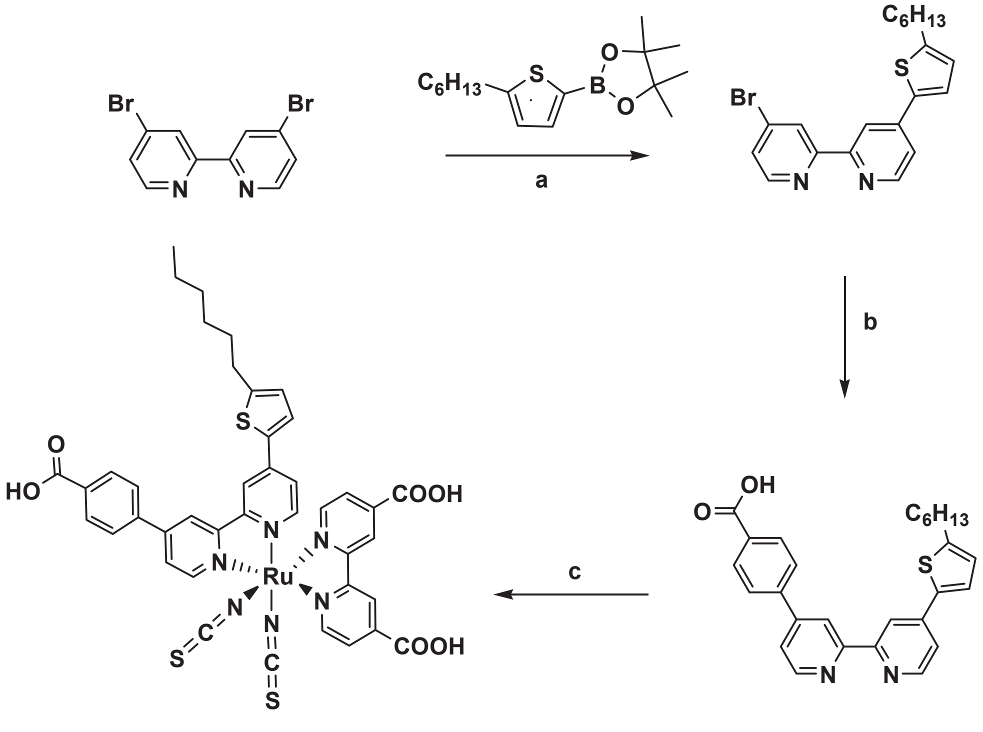


Figure S5. Comparison between absorption spectra on MC112 (black lines) and N719 (red lines) adsorbed on the TiO_2.

Synthesis:



MC112

Scheme S1. Synthesis of sensitizers MC112. Reagents and conditions: a) Pd(dppf)$_2$Cl$_2$, KF, KOAc, DMF, 85^0 C; b) ArB(OH)$_2$, Pd(PPh$_3$)$_4$, 2M Na$_2$CO$_3$, DME, 90^0 C; c) Ru(P-cymene)$_2$Cl$_2$, DMF, 60^0 C then Bipyridine dicarboxylic acid, NH$_4$SCN, 150^0 C.

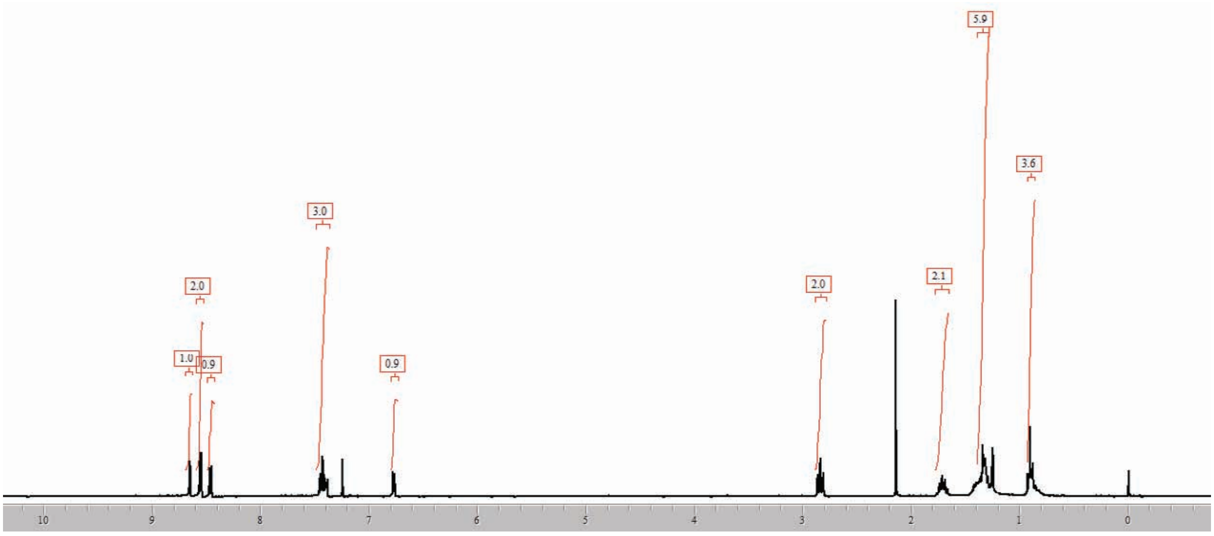


Figure S6. 1HNMR of 4-bromo-4’-(5-hexylthiophen-2-yl)-2,2’-bipyridine (1a).

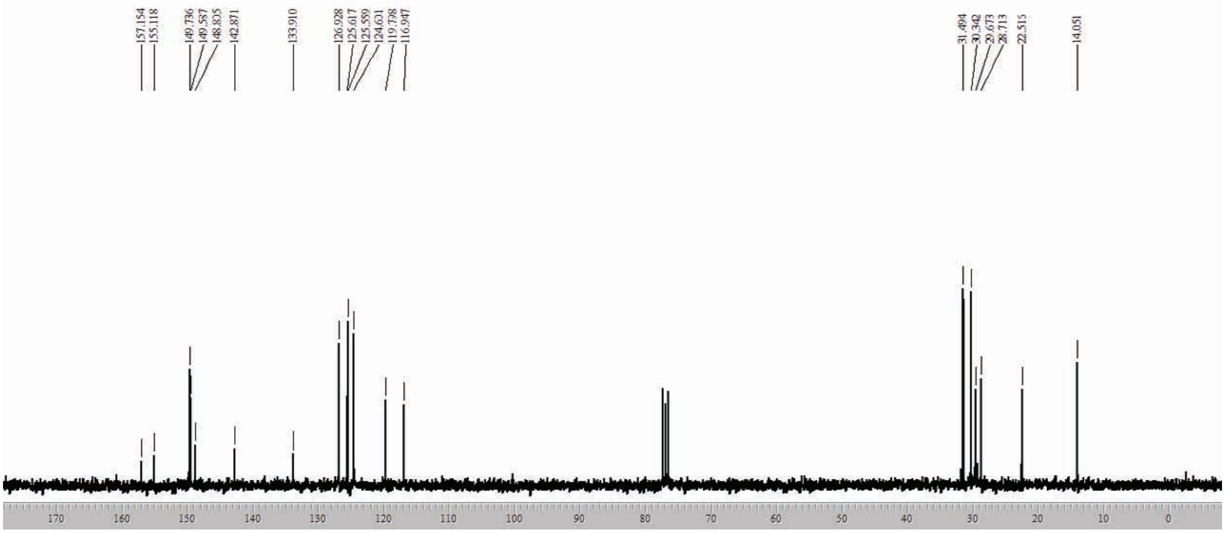


Figure S7. 13CNMR of 4-bromo-4’-(5-hexylthiophen-2-yl)-2,2’-bipyridine (1a).

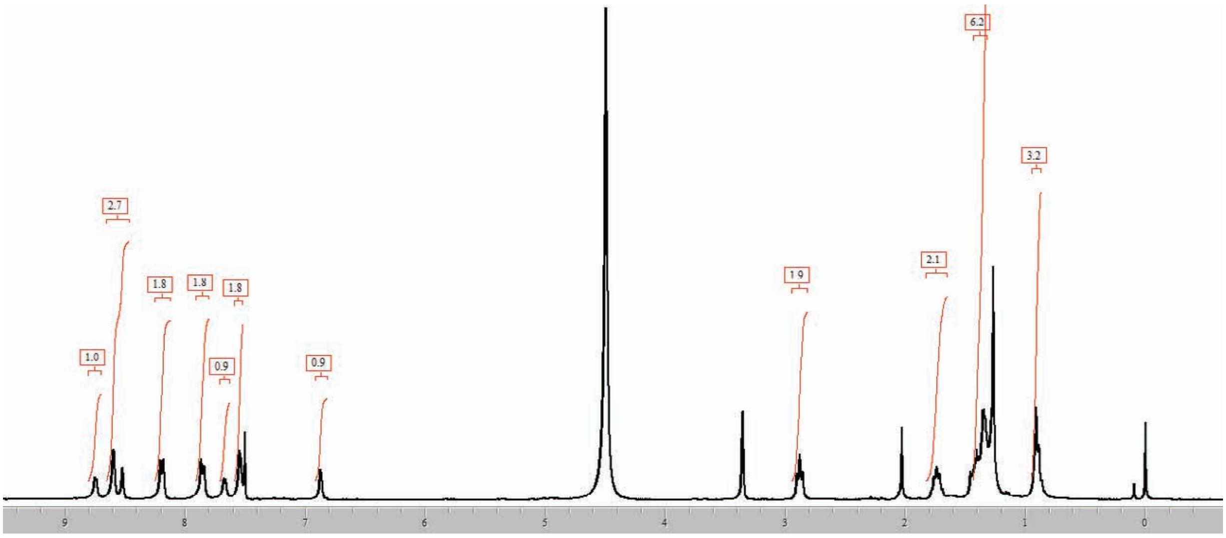


Figure S8. 1HNMR of 4-(2-(4-(5-hexylthiophen-2-yl)pyridin-2-yl)pyridin-4-yl)benzoic acid (1b).

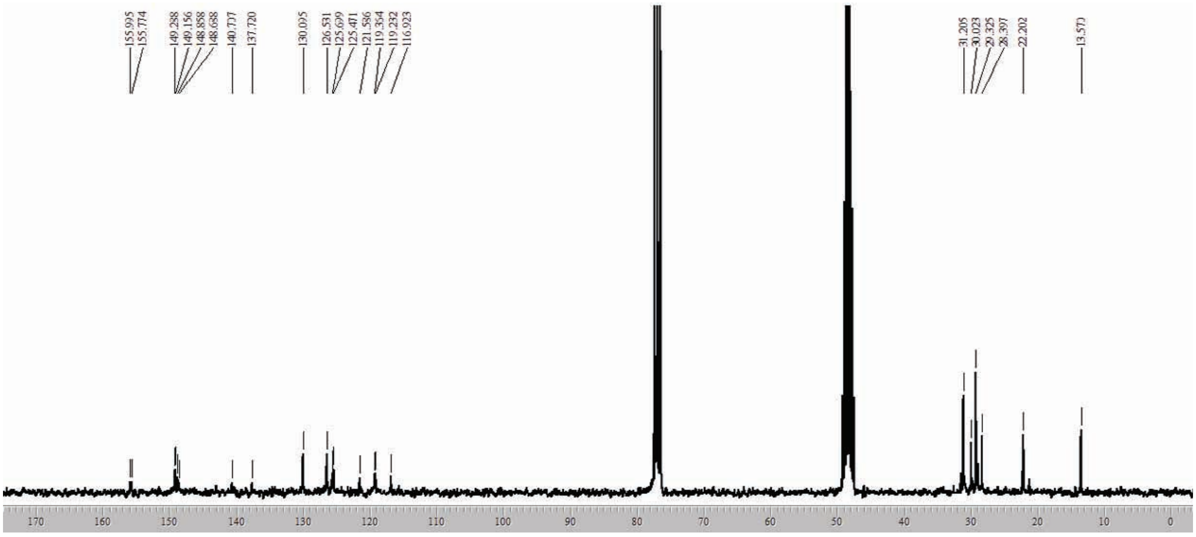


Figure S9. 13CNMR of 4-(2-(4-(5-hexylthiophen-2-yl)pyridin-2-yl)pyridin-4-yl)benzoic acid (1b).

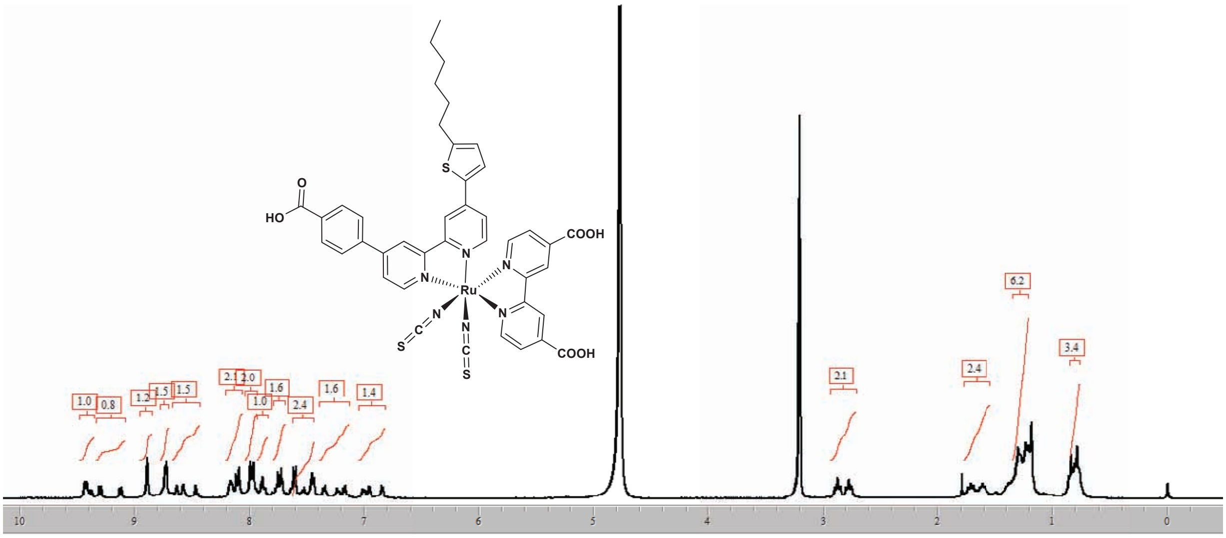


Figure S10. 1HNMR of **MC**112.

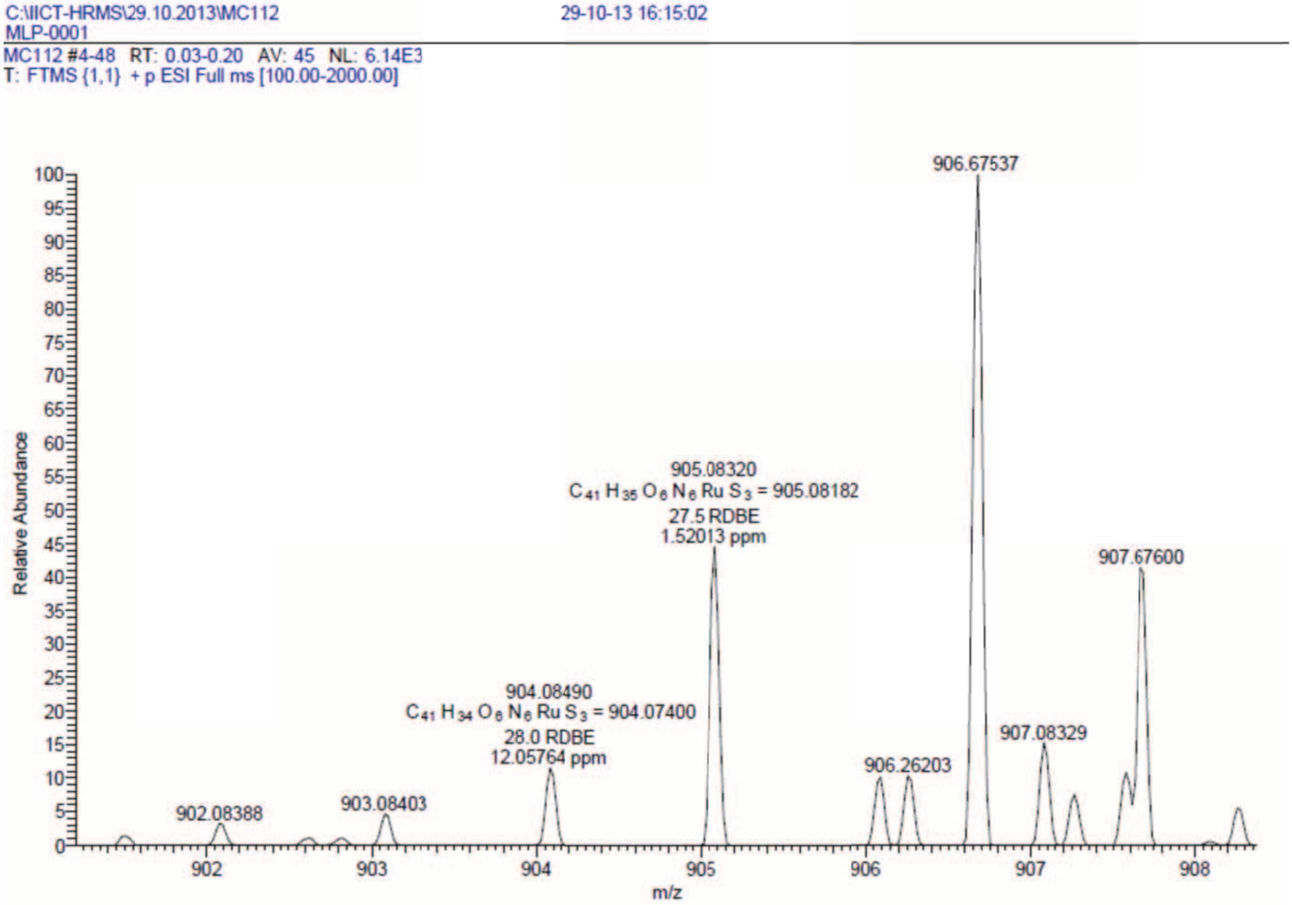


Figure 11. HMRS spectrum of the MC112 dye.

Table S1. Energies of the lowest unoccupied and highest occupied Kohn-Sham orbitals of MC112 triple protonated (3H), doubly protonated (2H), mono protonated, (1H) and doubly deprotonated (0H). Energy in eV.

	MC112_3H	MC112_2H	MC112_1H	MC112_0H
H-6	-6.94	-6.56	-6.41	-6.23
H-5	-6.88	-6.51	-6.40	-6.20
H-4	-6.38	-6.32	-6.25	-6.13
H-3	-6.25	-6.16	-6.08	-6.03
H-2	-5.80	-5.63	-5.50	-5.46
H-1	-5.74	-5.61	-5.49	-5.41
H	-5.52	-5.39	-5.24	-5.20
L	-3.15	-2.88	-2.68	-2.46
L+1	-2.82	-2.71	-2.23	-2.16
L+2	-2.58	-2.25	-2.20	-1.79
L+3	-2.32	-2.09	-1.83	-1.67
L+4	-2.18	-1.88	-1.36	-1.27
L+5	-1.95	-1.51	-1.31	-1.25
L+6	-1.29	-1.24	-1.15	-0.45

Table S2. Computed excitation energies (eV and nm) and oscillator strengths (*f*) for the optical transitions of MC112 in acetonitrile solution.

Complex	N_state	E (eV)	WL (nm)	f	Composition (%)	
MC112_3H	1	1.68	739	0.0279	H → L	90
	3	2.05	605	0.0979	H-2 → L H → L+1	47 40
	4	2.09	592	0.0386	H-2 → L H → L+1	36 49
	5	2.32	534	0.0945	H-2 → L+1 H-1 → L+1	25 57
	6	2.36	525	0.0493	H-2 → L+1 H-1 → L+1	63 11
	7	2.45	505	0.0668	H-1 → L+1 H → L+2	19 56
	9	2.61	476	0.0385	H-3 → L	81
	10	2.64	470	0.0516	H-2 → L+2	82
	11	2.70	460	0.0454	H → L+3 H → L+4	50 31
	12	2.77	447	0.0463	H → L+3 H → L+4	30 62
	14	2.90	427	0.0372	H-1 → L+3	82
	15	2.96	419	0.0198	H-3 → L+1 H-2 → L+3	62 18
	16	2.96	419	0.0180	H-3 → L+1 H-2 → L+3 H-2 → L+4	30 31 32
	18	3.00	413	0.0429	H-1 → L+4 H → L+5	39 47
	20	3.09	401	0.1271	H-5 → L	62

					H-4 → L+1	25
MC112_2H	1	1.87	664	0.0486	H → L	86
	2	2.01	618	0.0382	H → L+1	76
	4	2.17	571	0.1160	H-2 → L	71
	5	2.20	563	0.0401	H-1 → L+1	74
	6	2.36	525	0.0707	H-2 → L+1	60
	7	2.64	470	0.0726	H → L+2 H → L+3	72 23
	8	2.73	455	0.0538	H → L+2 H → L+3	18 66
	9	2.82	440	0.0290	H-3 → L	84
	10	2.85	434	0.0251	H-1 → L+2	72
	11	2.88	430	0.0428	H-1 → L+2	67
	12	2.90	427	0.0137	H-1 → L+3	62
	13	2.92	424	0.0283	H → L+4	80
	15	2.97	417	0.0426	H-3 → L+1	93
	16	3.04	409	0.0331	H-4 → L	90
MC112_1H	1	1.90	651	0.0482	H → L	83
	3	2.23	556	0.1299	H-2 → L H → L+1	56 20
	4	2.30	539	0.0314	H → L+1 H → L+2	41 34
	5	2.51	493	0.0134	H-1 → L+1 H-1 → L+2	46 19
	6	2.55	487	0.1094	H → L+1 H → L+2	21 55
	7	2.67	465	0.1286	H-2 → L+1	47
	8	2.77	448	0.0190	H-1 → L+1 H-1 → L+2	30 56
	10	2.82	439	0.0235	H-2 → L+2 H → L+3	20 69
	11	2.93	423	0.0259	H-3 → L	96
MC112_0H	1	2.02	613	0.0269	H → L	92
	3	2.30	539	0.0562	H → L+1	80
	4	2.38	522	0.1480	H-2 → L H-1 → L	34 40
	6	2.67	464	0.0868	H-2 → L+1	80
	7	2.85	436	0.0192	H → L+2	78
	8	2.96	419	0.1206	H → L+3	77
	9	3.04	407	0.0676	H-1 → L+2	75
	10	3.07	404	0.0368	H-3 → L	90
	11	3.09	401	0.0667	H-2 → L+2	86

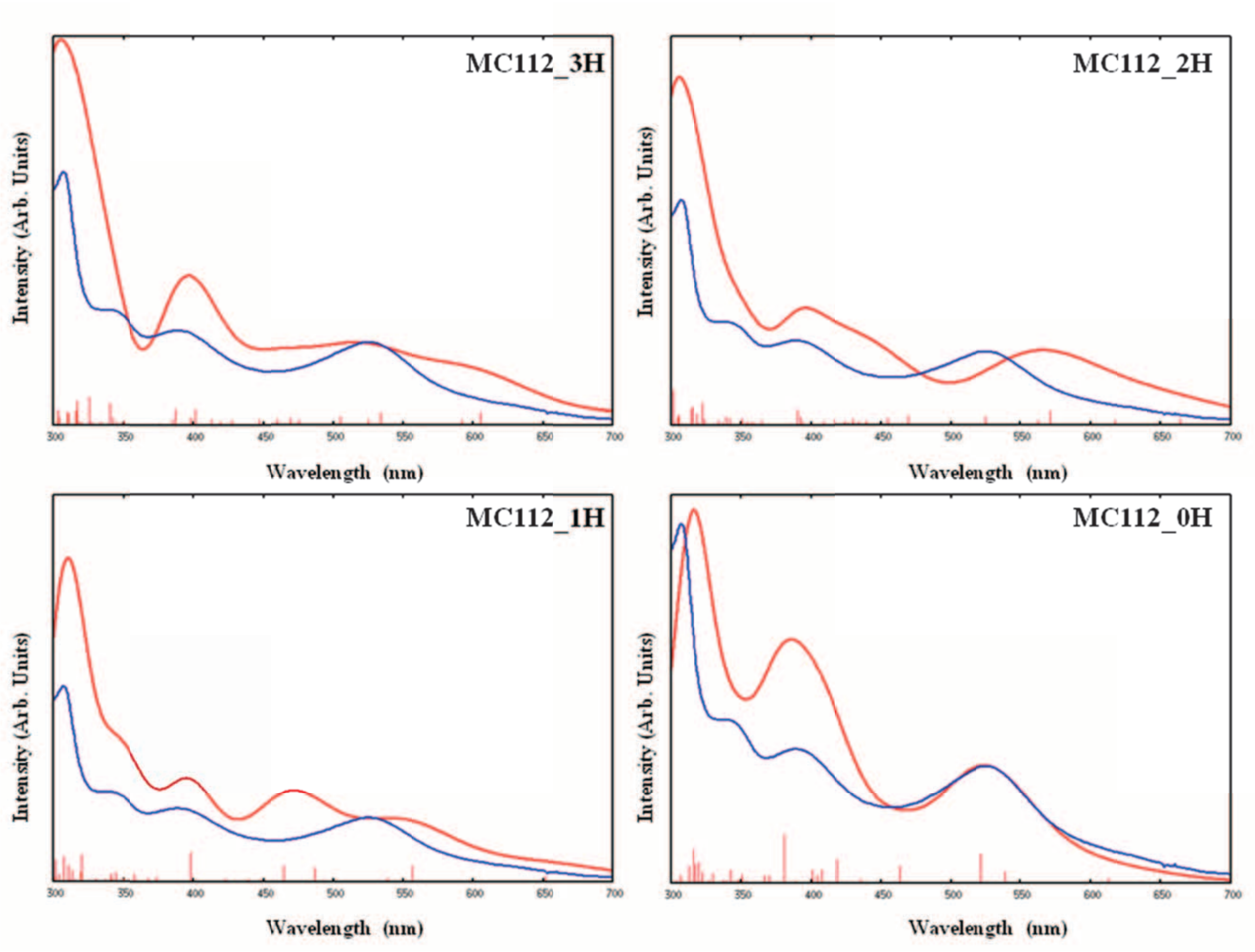


Figure S12. Comparison between computed (red lines) and experimental (blue lines) absorption spectra of **MC112** in acetonitrile. Red vertical lines correspond to calculated excitation energies and oscillator strengths for the various protonated forms calculated for the **MC112** dye.

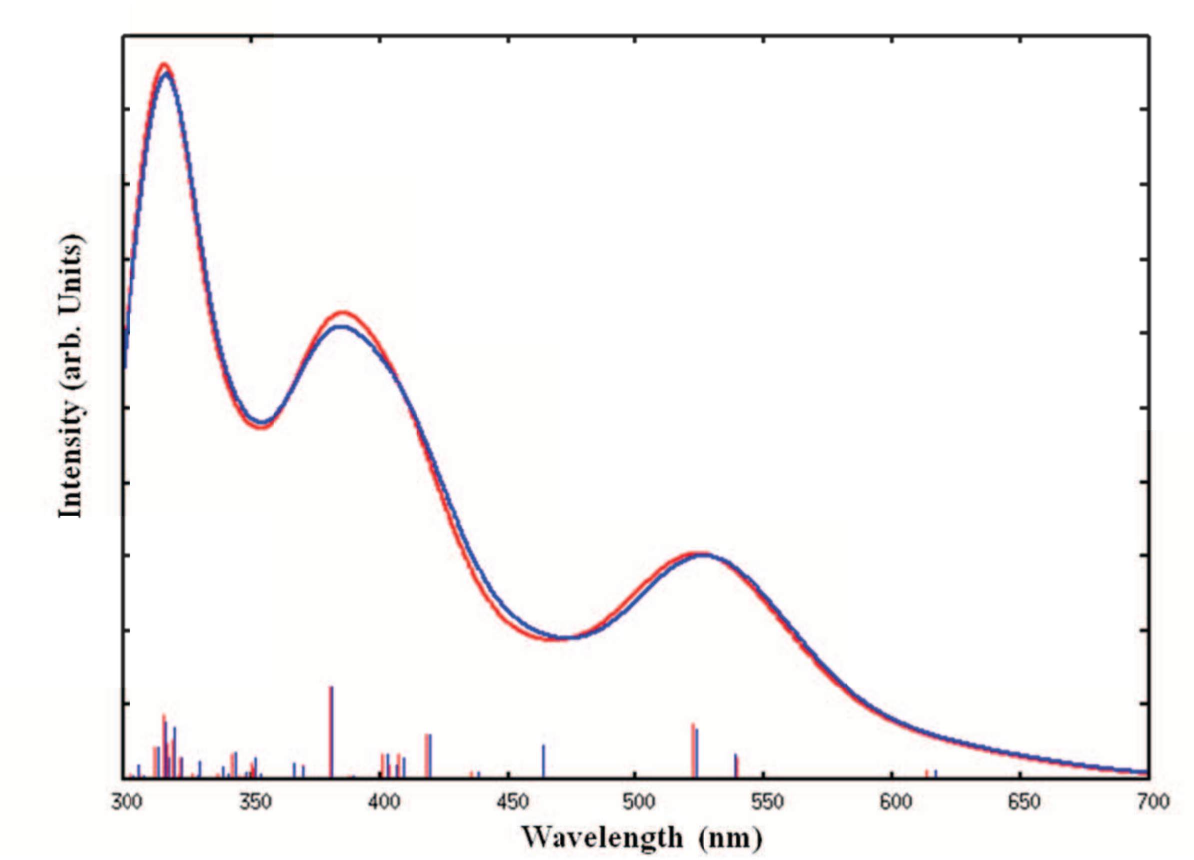


Figure S13. Comparison between computed absorption spectra of the totally deprotonated **MC112** in acetonitrile (red lines) and ethanol (blue lines) solution. Red and blue vertical lines correspond to calculated excitation energies and oscillator strengths for the **MC112** dye in acetonitrile and ethanol solution, respectivelly.

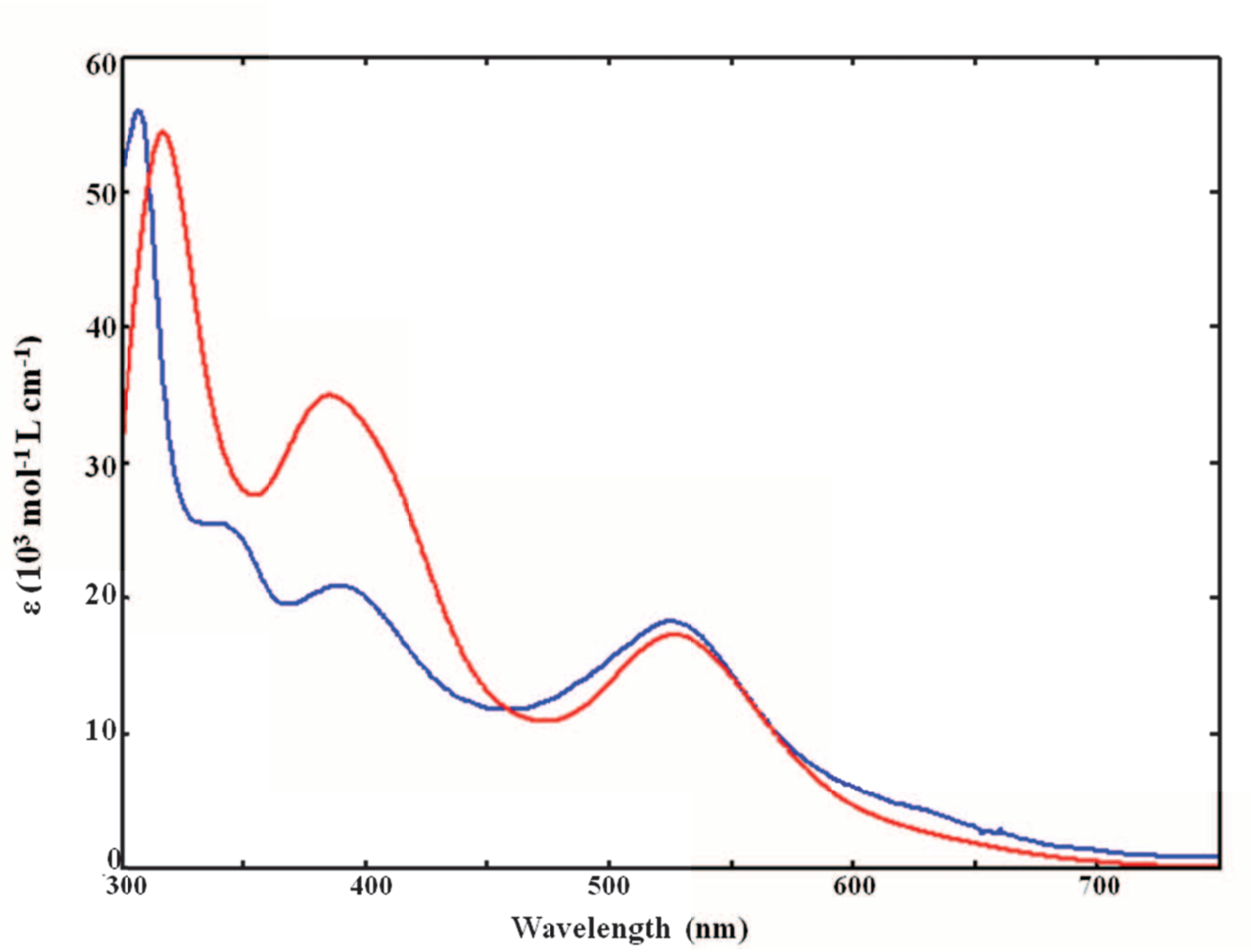


Figure S14. Comparison between computed (red lines) and experimental (blue lines) absorption spectra of totally deprotonated **MC112_A** in acetonitrile.

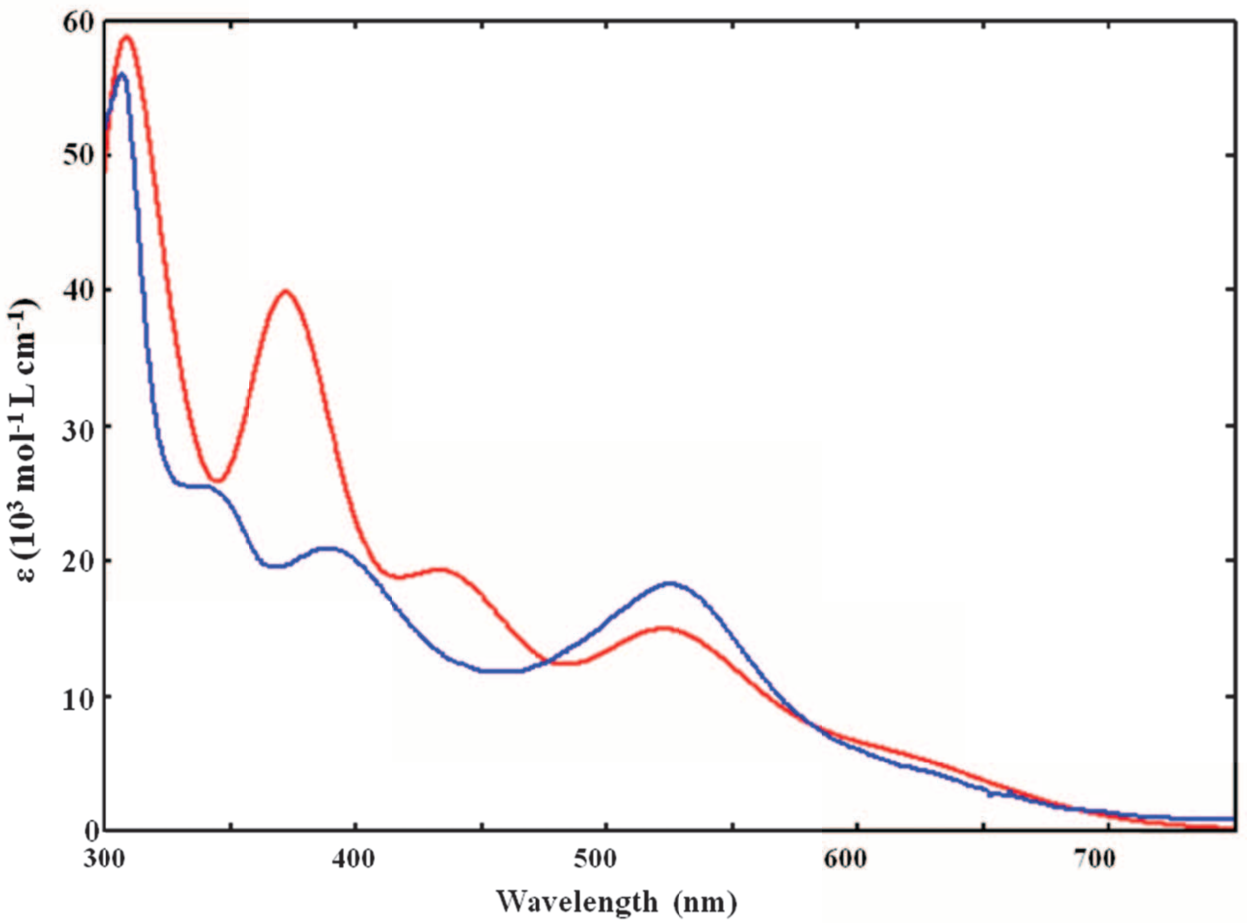


Figure S15. Comparison between computed (red lines) and experimental (blue lines) absorption spectra of totally deprotonated **MC112_B** in acetonitrile.

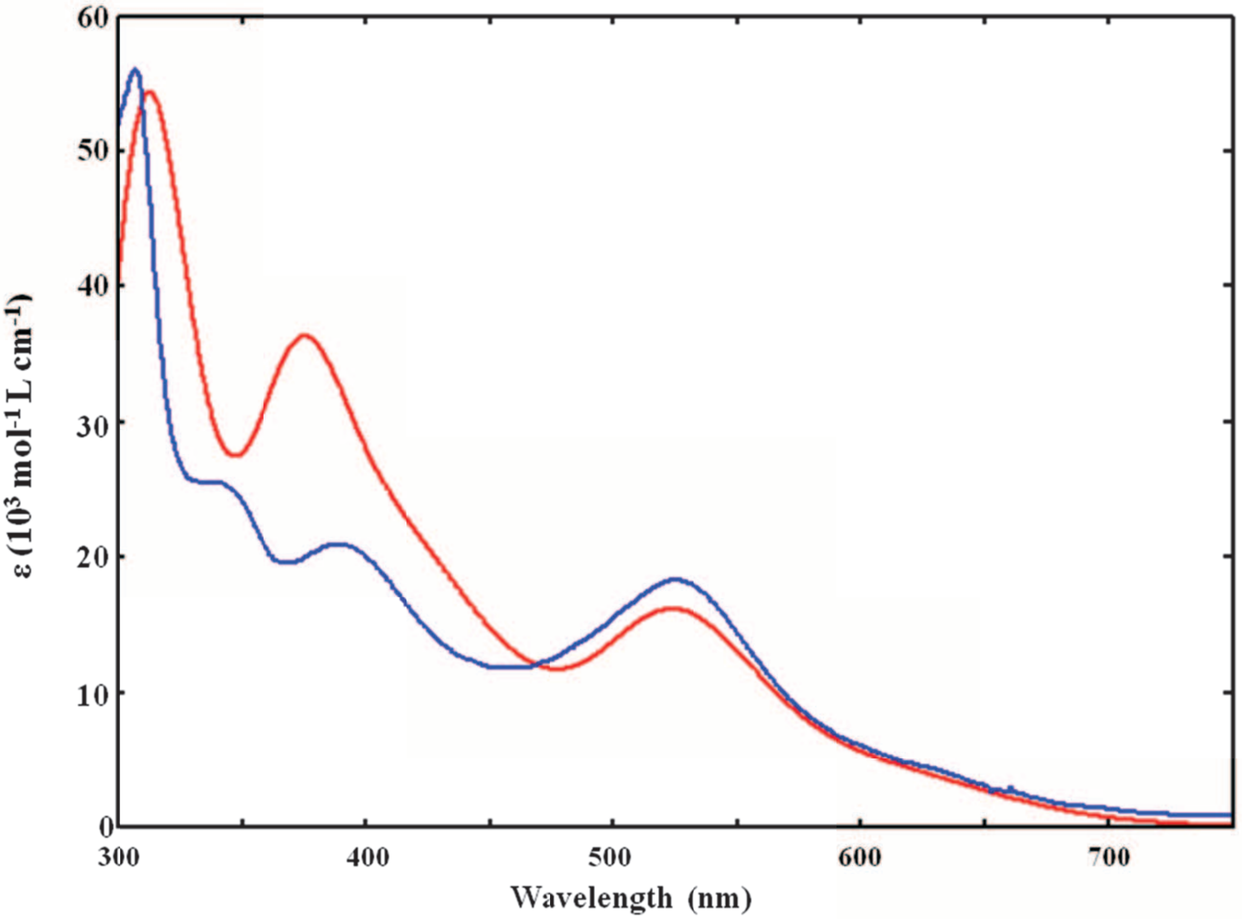


Figure S16. Comparison between experimental (blue lines) and computed (red lines) absorption spectra of totally deprotonated **MC112** in acetonitrile. The computed spectra is the average of the isomers A and B.

References:

1. G. Pizzoli, M. G. Lobello, B. Carlotti, F. Elisei, M. K. Nazeeruddin, G. Vitillaro and F. De Angelis, *Dalton Trans.*, 2012, **41**, 11841-11848.