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Nonlinear optical-active ferrocene conjugated Y-shaped imidazole donor-π-acceptor [(D-π)$_2$-IM-π-A] compounds for dye-sensitized solar cells using non-corrosive copper complexes as a redox mediator

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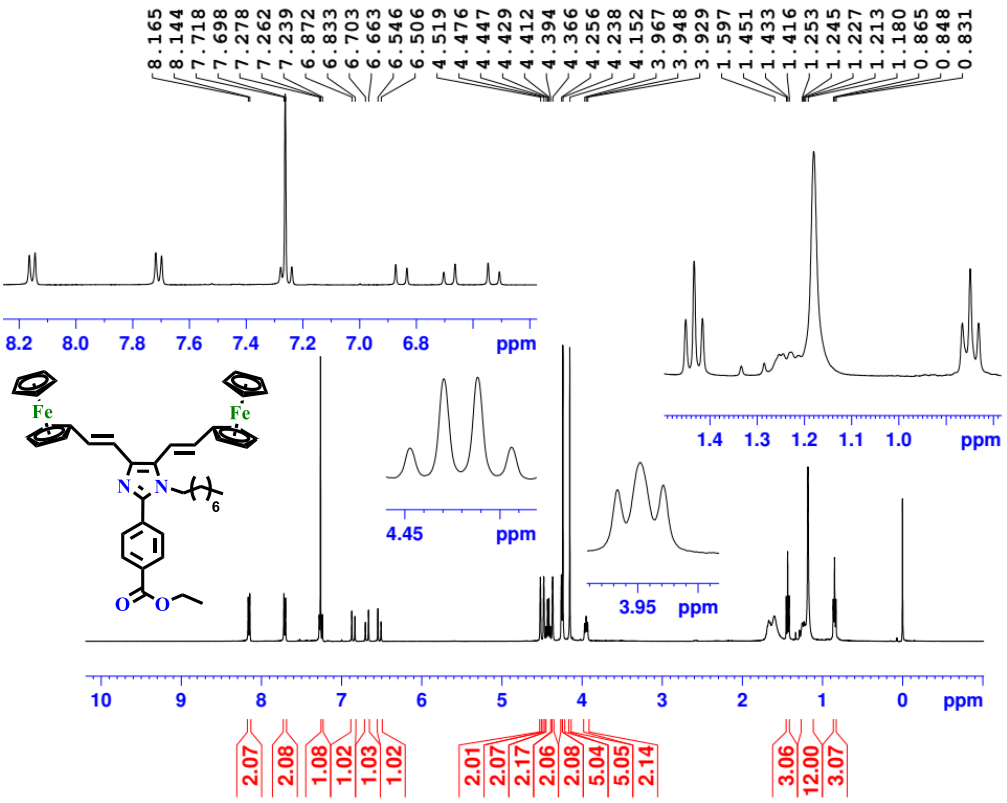


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$ at 25 °C.

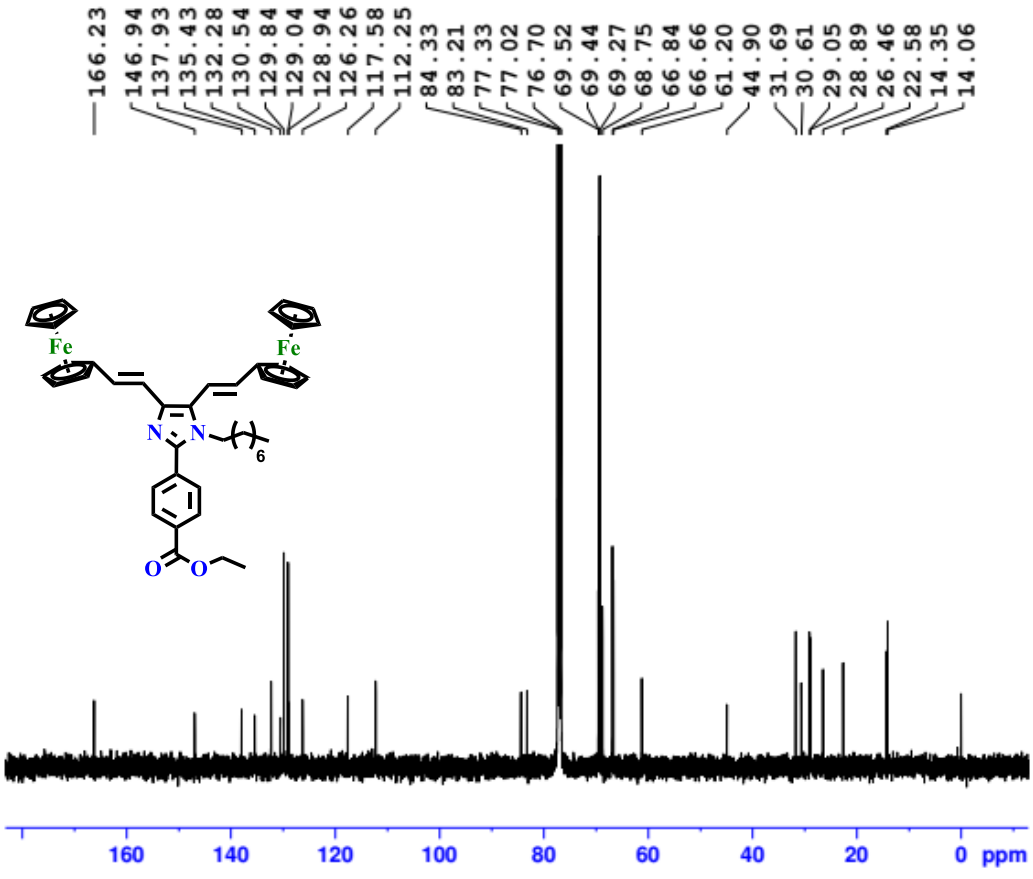


Figure S2. ^{13}C NMR spectrum of compound **1** in $CDCl_3$ at 25 °C.

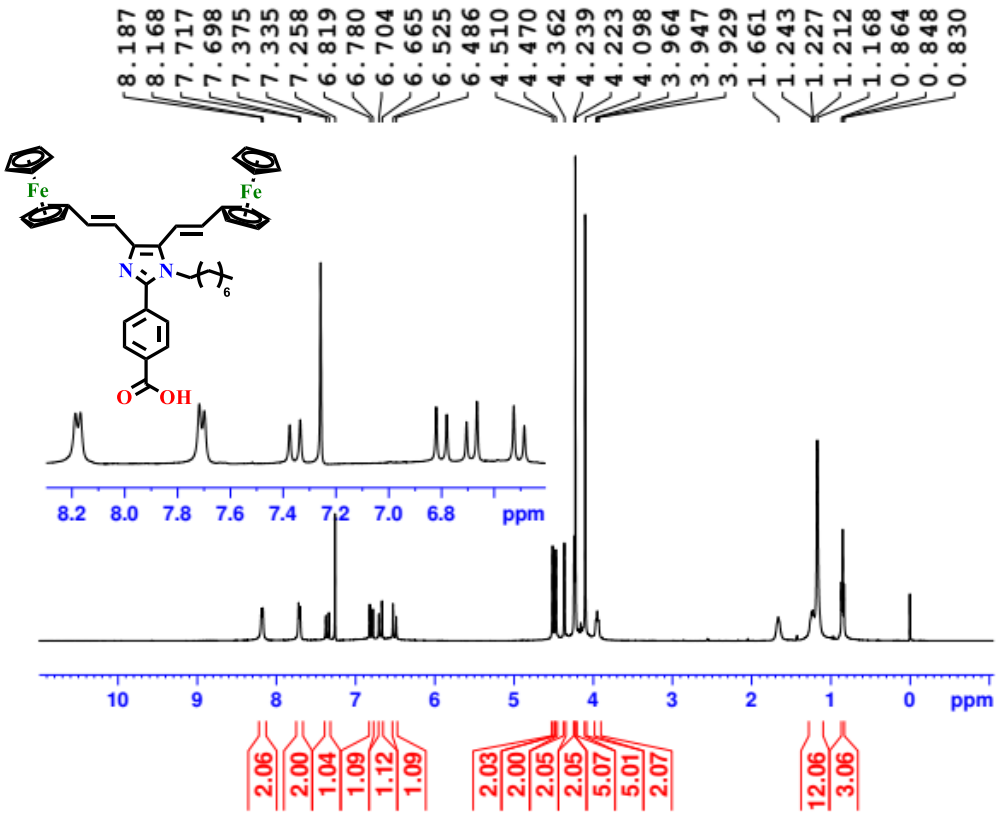


Figure S3. ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at 25 °C.

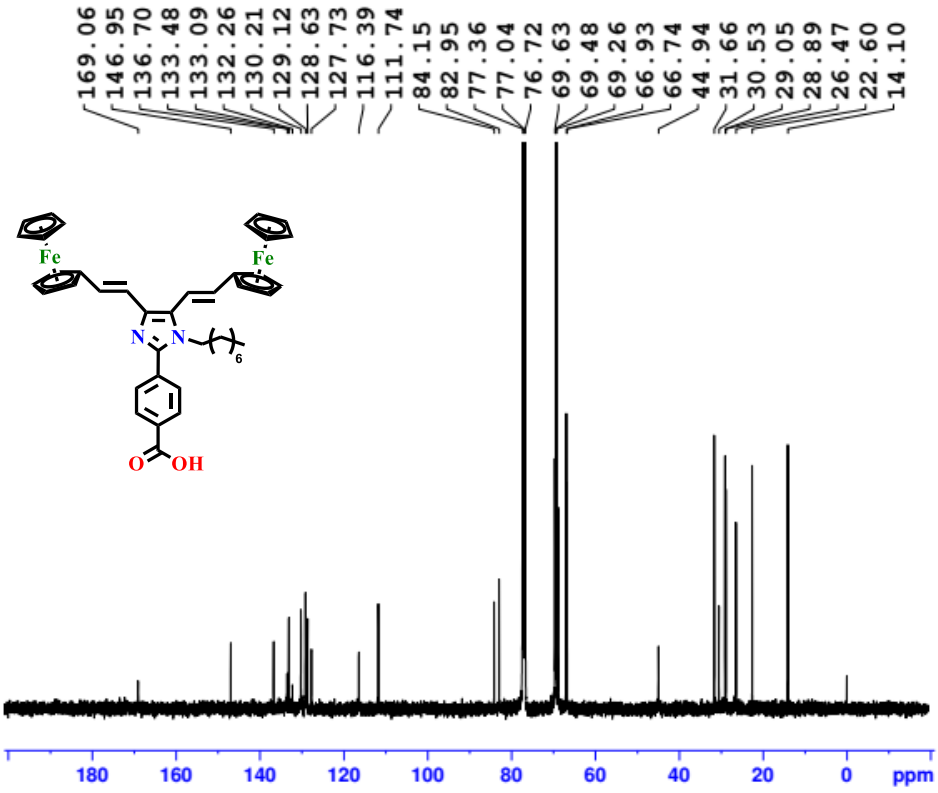


Figure S4. ^{13}C NMR spectrum of compound **2** in $CDCl_3$ at 25 °C.

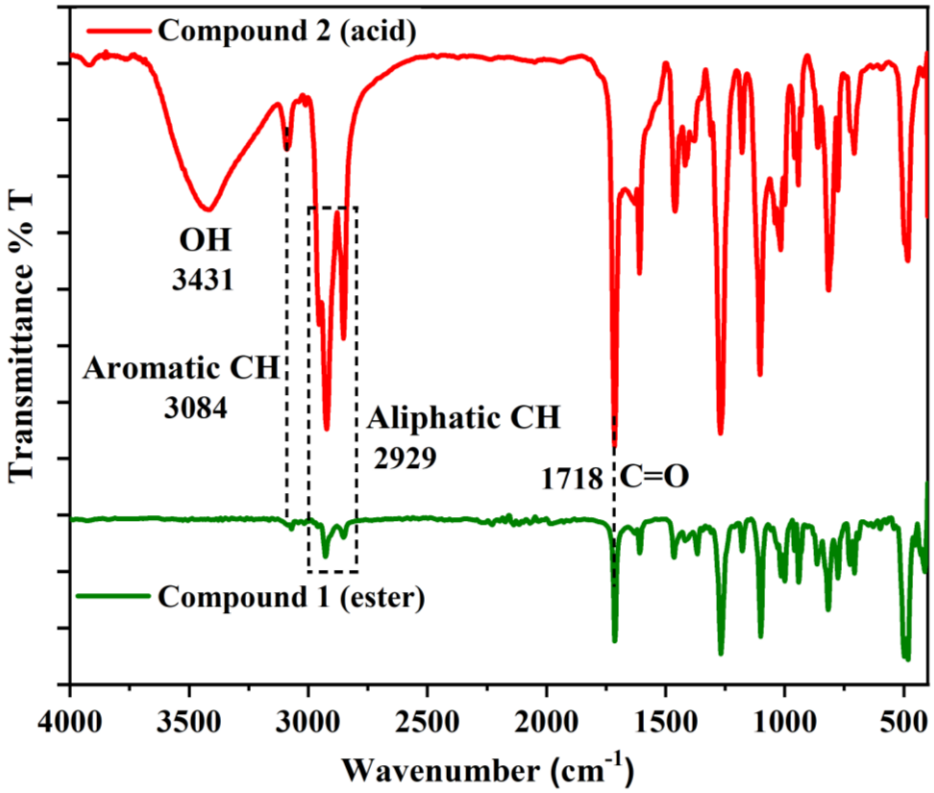


Figure S5. FT-IR spectra for compounds **1** and **2**.

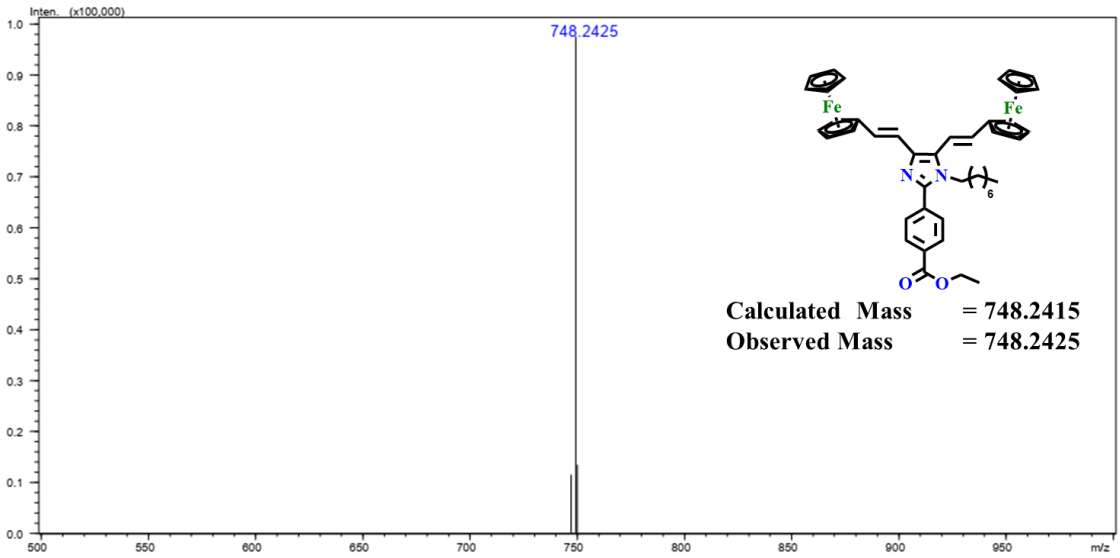


Figure S6. ESI-Mass spectrum of compound **1**.

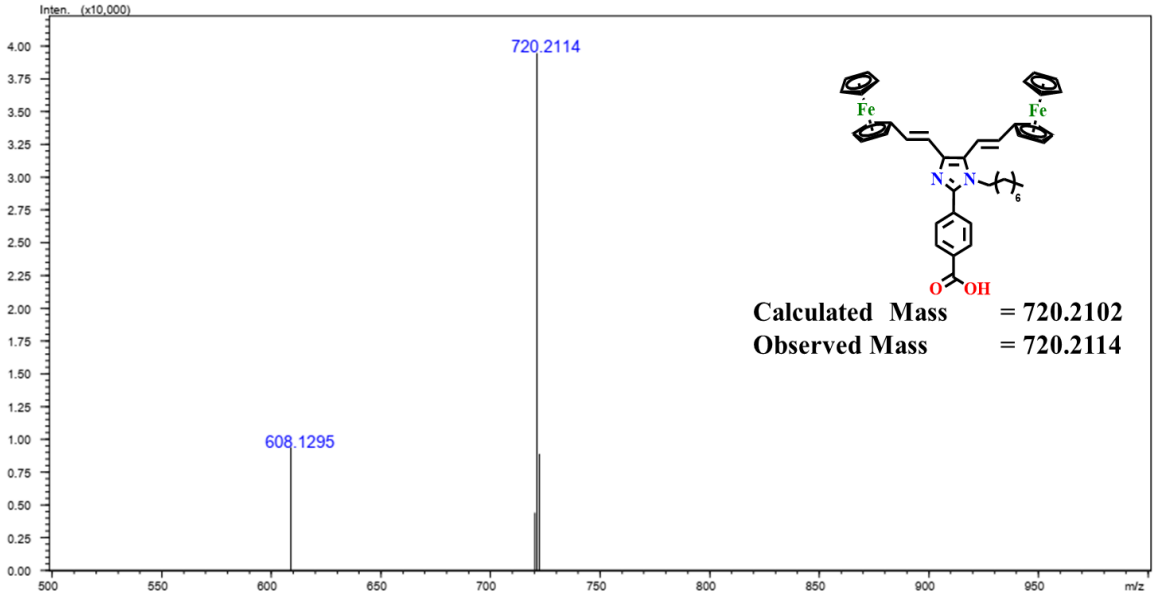


Figure S7. ESI-Mass spectrum of compound **2**.

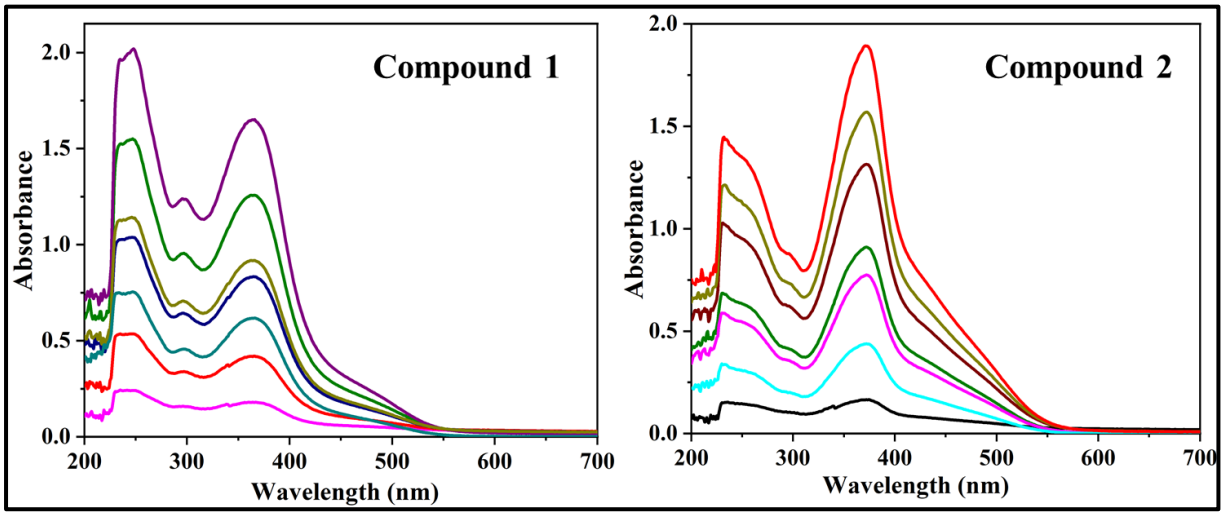


Figure S8. Absorption spectra of compounds **1** and **2** in CH_2Cl_2 solution using different concentrations.

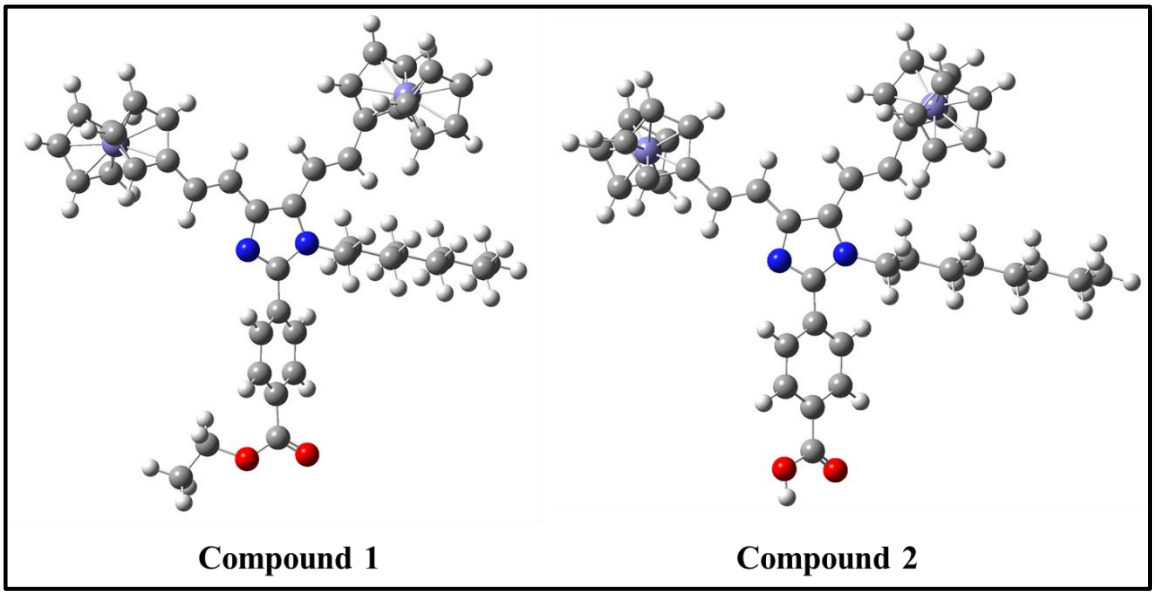


Figure S9. The optimized geometries of compounds **1** and **2** obtained at B3LYP/6-31+G** level of theory

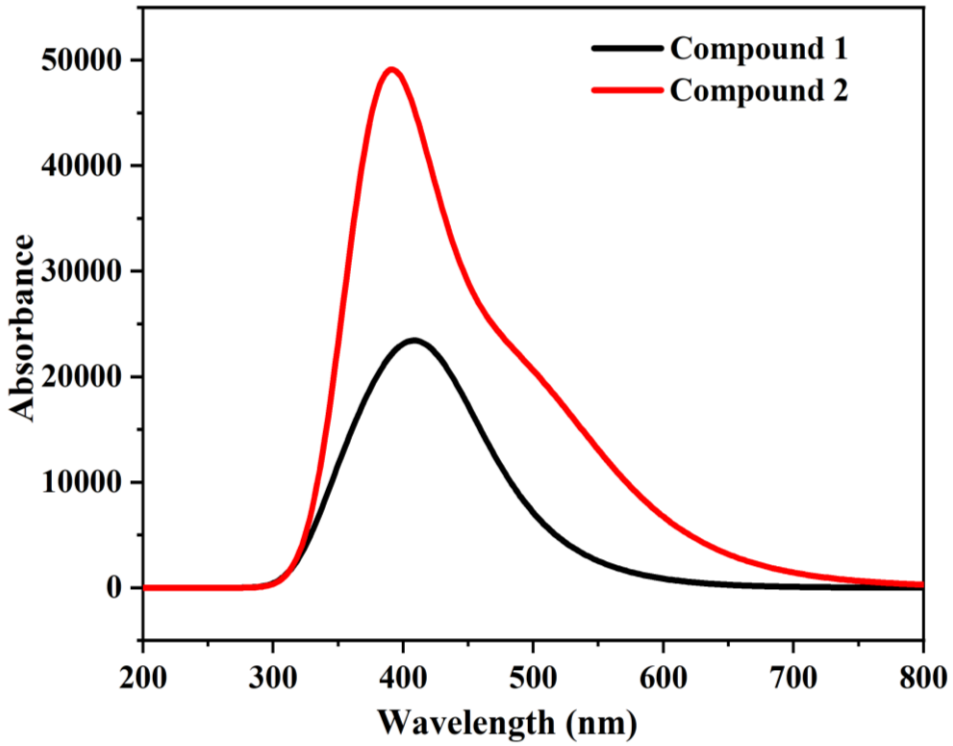


Figure S10. Theoretically calculated absorption spectra for compounds **1** and **2**. The absorption spectra were obtained by TD-DFT (dichloromethane solvent) with B3LYP/6-31+G** level of theory.

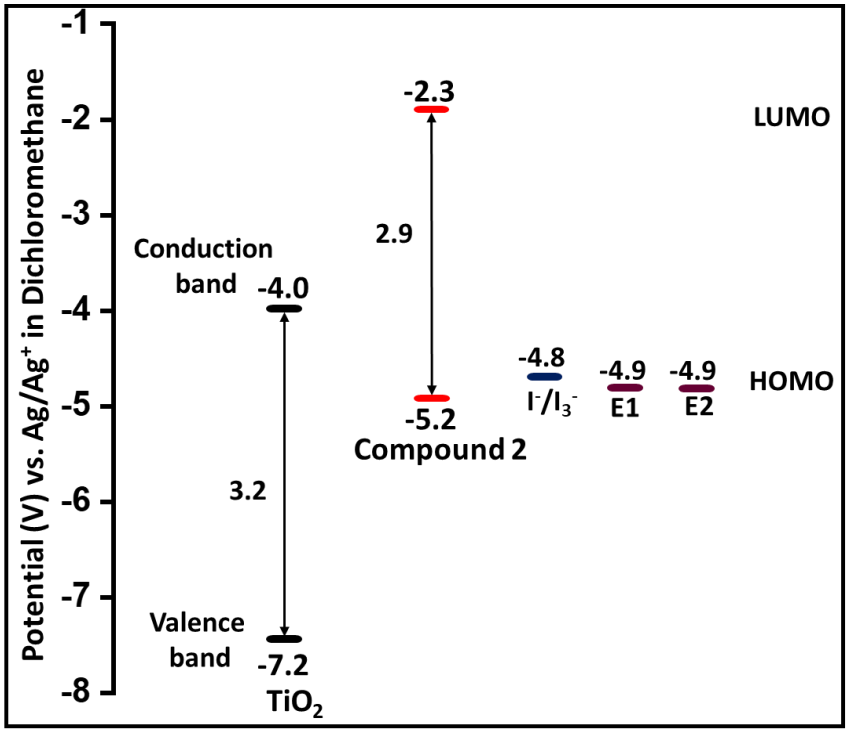


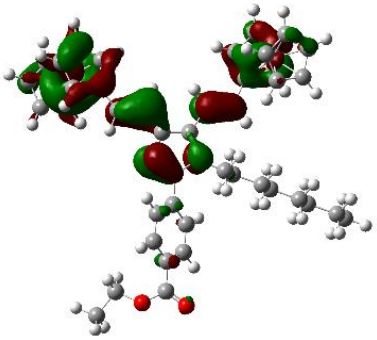
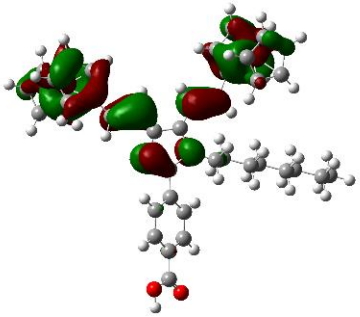
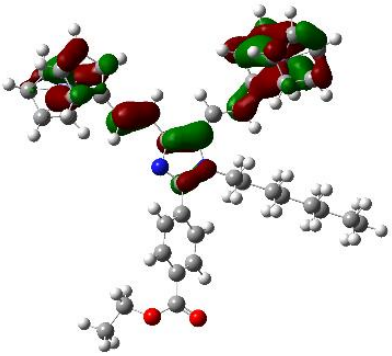
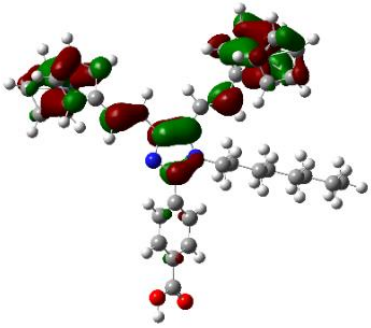
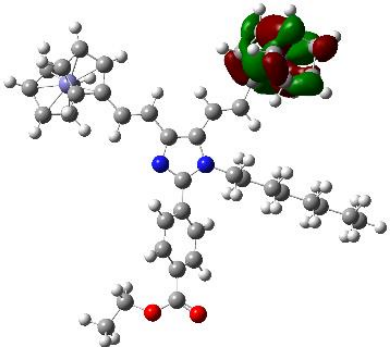
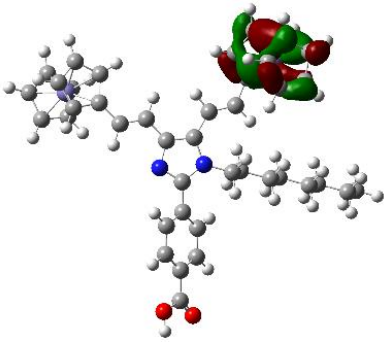
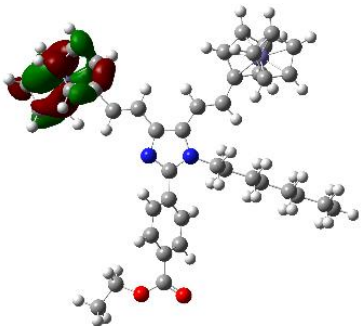
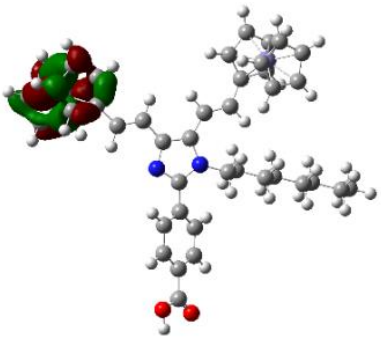
Figure S11. The energy level diagram of compound **2** including the conduction band of TiO_2 and redox couples.

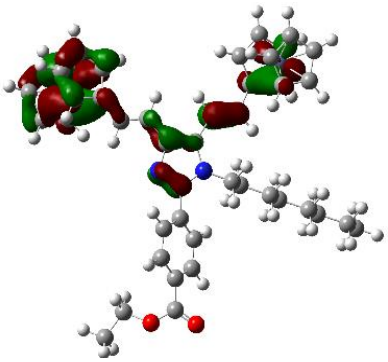
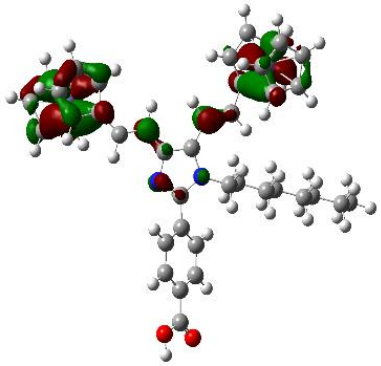
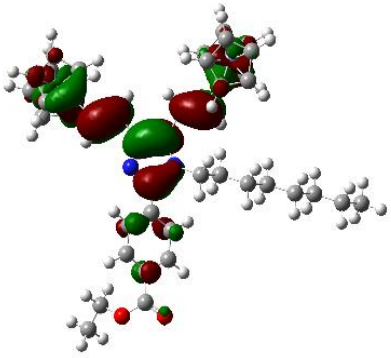
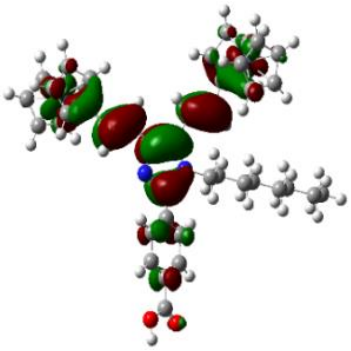
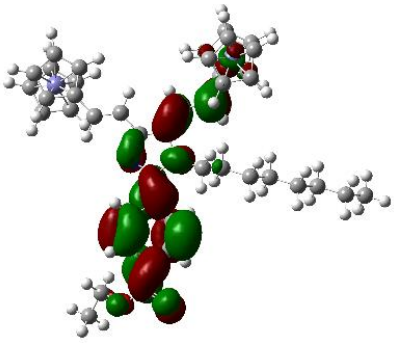
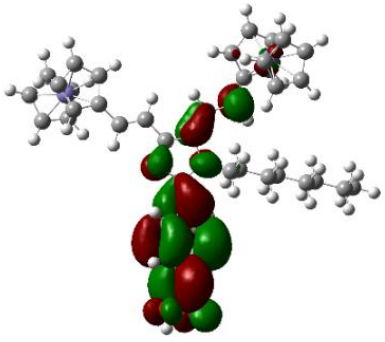
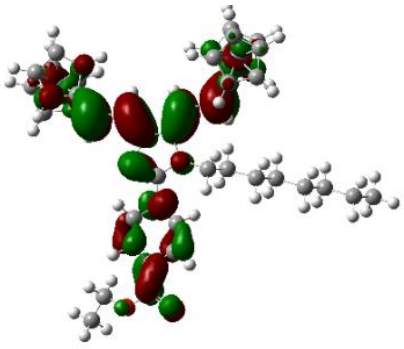
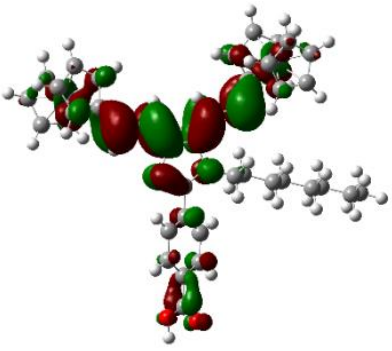
Table S1. Selected transitions obtained from TD-DFT calculation with B3LYP/6-31+G** level theory

Entry	λ (nm)	Oscillator strength, *f*	Energy (eV)	Selected Major Transitions[a]
1 (ester)	408	0.3995	3.33	H → L+1 (40%)
	447	0.3425	2.76	H → L (91%)
	386	0.2822	3.20	H → L+1 (38%)
	388	0.0394	3.18	H-2 → L (52%)
	571	0.0263	2.16	H-3 → L+4 (16%)
	375	0.0254	3.30	H-1 → L+1 (27%), H-6 → L+6 (16%)
	495	0.0214	2.50	H-6 → L+3 (12%)
	354	0.0198	3.49	H-4 → L (52%)
2 (acid)	390	0.5224	3.17	H → L+1 (36%),
	395	0.3520	3.13	H → L+1 (36%)
	483	0.3041	2.56	H → L (73%)
	379	0.1616	3.26	H-2 → L+5 (17%), H-1 → L+1 (17%)
	371	0.1132	3.33	H-4 → L (21%), H-3 → L+4 (14%)
	499	0.1073	2.48	H-5 → L+4 (33%), H → L (19%)
	409	0.0337	3.02	H-1 → L (90%)
	377	0.0211	3.28	H-2 → L+1 (31%)
	495	0.0181	2.50	H-2 → L+5 (32%)
	344	0.0134	3.59	H-1 → L+1 (46%), H → L+3 (18%)

[a] H = HOMO; L = LUMO; only contributions above 10% are included.

Table S2. Density surfaces of the frontier orbitals involved in electronic transitions of compounds **1** and **2** which is derived from B3LYP/6-31+G** level of theory using isosurface value of 0.02 au.

Orbitals	1	2
HOMO-5		
HOMO-4		
HOMO-3		
HOMO-2		

HOMO-1		
HOMO		
LUMO		
LUMO+1		

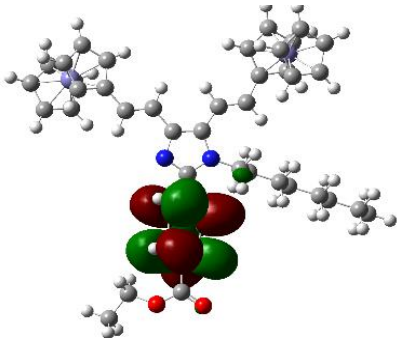
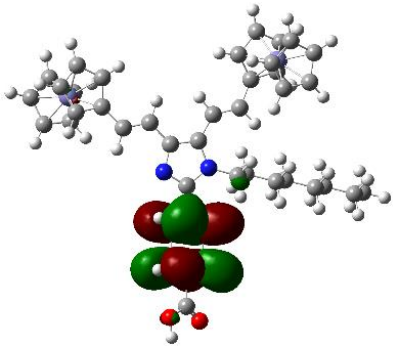
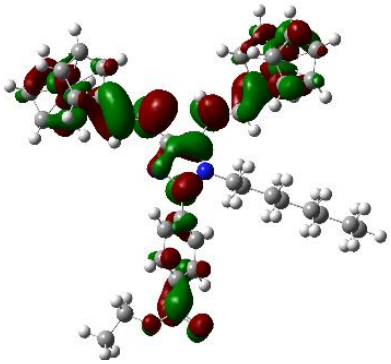
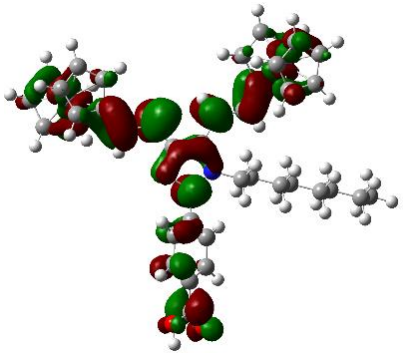
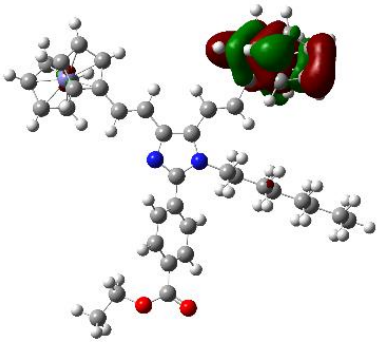
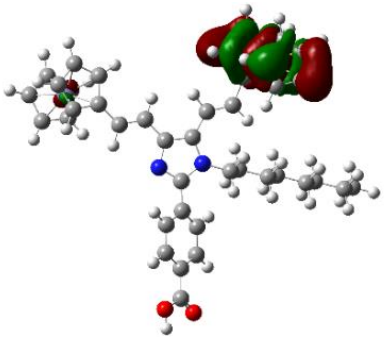
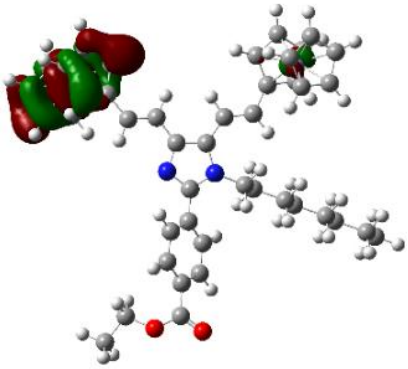
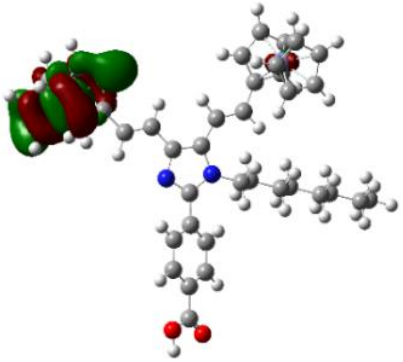
LUMO+2		
LUMO+3		
LUMO+4		
LUMO+5		

Table S3. DSSC performance of some previously reported ferrocene (Fc) based sensitizers

Dye	***Jsc*** **($mAcm^{-2}$)**	***Voc*** **(V)**	**FF**	***η*** **(%)**	**Redox mediator**	**Ref**
Fc-dithiocarbamates 1	5.72	−0.74	0.74	3.14		
2	5.09	−0.74	0.74	2.80		
3	4.74	−0.74	0.73	2.59		
4	7.14	−0.74	0.73	3.87		
5	6.41	−0.74	0.72	3.46		
6	6.83	−0.74	0.73	3.69	I^-/I_3^-	1
Fc-triphenylamine D1	8.13	0.66	0.68	3.65		
D2	9.84	0.72	0.70	4.96	I^-/I_3^-	2
Fc-diketopyrrolopyrrole						
P:SM1	11.34	0.98	0.58	6.44		
P:SM2	12.66	0.88	0.62	6.89	I^-/I_3^-	3
Fc-benzimidazole NO_2	9.75	-0.628	0.61	3.71		
COOH	12.74.	-0.648	0.70	5.81	I^-/I_3^-	4
Fc-diketenone	2.56	-0.552	0.57	0.81		
Fc-Quinoxaline	3.57	-0.576	0.59	1.22		
Fc-Quinoxaline-Cl	5.14	-0.630	0.61	1.97		
Fc-Quinoxaline-NO2	7.38	-0.642	0.71	3.38		
Fc-Quinoxaline-COOH	9.14	-0.646	0.71	4.42	I^-/I_3^-	5
Fc-D1 (AN-50)	0.730	0.407	0.584	0.180		
Fc-D1 (Hybrid)	0.610	0.405	0.612	0.160		
Fc-D2 (AN-50)	0.590	0.337	0.579	0.115		
Fc-D2 (Hybrid)	0.380	0.770	0.603	0.190		
Fc-D3 (AN-50)	1.070	0.434	0.575	0.270		
Fc-D3 (Hybrid)	1.190	0.494	0.541	0.325	I^-/I_3^-	6
Ferrocenyl cyanoviny 1	0.41	0.763	35	0.10		
2	0.039	0.841	28	0.009	I^-/I_3^-	7
Ferrocenyl azine Fc-OH	12.91	0.710	0.64	5.88		
Fc-NO_2	9.21	0.690	0.63	4.04	I^-/I_3^-	8
$FcCH=NC_6H_4COOH$ (1)	8.28	-0.648	0.71	0.81		
$FcCH=NCH_2CH_2OH$ (2)	7.24	-0.660	0.67	0.68		
Fc-CHO (3)	7.60	-0.640	0.71	0.73	I^-/I_3^-	9
Fc-Multi donor systems						
Dye 1	0.025	0.211	0.318	0.0017		
Dye 2	0.049	0.282	0.347	0.0047		
Dye 1 + CDCA	0.071	0.388	0.452	0.012		
Dye 2 + CDCA	0.086	0.428	0.432	0.015	I^-/I_3^-	10
Fc-modified zinc phthalocyanine	0.014	45	0.48	0.003	I^-/I_3^-	11
Fc-chalcones Fc1	0.606	0.593	58.70	0.211		
Fc2	0.776	0.601	52.70	0.246	I^-/I_3^-	12
Ferrocene appended porphyrin F3P	0.068	0.283	0.42	0.008	Co(II)/Co(III)	13
	1.51	**0.40**	**42.7**	**0.26**	**I^-/I_3^-**	
Y-shaped imidazole acid	**1.18**	**0.41**	**39.1**	**0.19**	**Cu(I)/Cu(II)**	**This**
(compound **2**)	**0.95**	**0.40**	**40.6**	**0.16**	**Cu(I)/Cu(II)**	**work**

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