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Supporting Information for

Molecular Design and Synthesis of Ruthenium(II) Sensitizers for Highly Efficient Dye-sensitized Solar Cells

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Synthesis precursor compounds

3,4-dihexylthiophene-2-carbaldehyde (2)

3,4-dihexylthiophene (**1**) was synthesized according to the literature.[1] **1** (3.0 g, 11.88 mmol) and DMF (0.9 g, 12.32 mmol) were dissolved in 1,2-dichloromethane (50 mL). After the solution was cooled to 0 °C, phosphorus oxychloride (1.82 g, 11.88 mmol) was added dropwise and stirred for 30 min. Then, the solution was refluxed at 65 °C for 4 h under nitrogen and cooled to room temperature. It was neutralized with sodium acetate and extracted with dichloromethane. After the solvent is removed, the residue was loaded onto silica gel column with hexane as an eluent to give yellow oil (2.9 g). Yield: 87%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.03 (s, 1H), 7.35 (s, 1H), 2.90 (t, J = 7.6 Hz, 2H), 2.55 (t, J = 7.6 Hz, 2H), 1.66-1.32 (m, 16H), 0.92 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 182.60; 151.47; 144.40; 138.21; 130.22; 31.80; 31.64; 31.53; 29.77; 28.27; 27.03; 22.58; 22.54; 14.35; 14.01.

4,4′-Bis(diethylphosphonomethyl)-2,2′-bipyridine (3)

3 was synthesized according to the literature.[2,] A solution of 4,4'-bis(bromomethyl)-2,2′-bipyridine (2 g, 7.60 mmol) and triethylphosphite (5 mL, 0.29 mol) was heated at 80 ºC for 6 h. After the solution was cooled to room temperature, triethylphosphite was removed under reduced pressure and washed with pentane (20 mL). The residue was dissolved in CH_2Cl_2 and purified by column chromatography (silica gel, acetone) and dried to give a pale yellow solid. Yield: 95 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (d, J = 5.1 Hz, 2H), 8.33 (s, 2H), 7.32 (d, J = 5.1 Hz, 2H), 4.07 (dq, 8H), 3.23 (d, J = 22.2 Hz, 4H), 1.27 (t, J = 7.2 Hz, 12H).

3-Hexylthiophene-2-carbaldehyde (5).

2-bromo-3-hexylthiophene (**4**) was synthesized according to the literature.[3] Under nitrogen atmosphere, butyllithium (7.28 mL, 5.83 mmol, 1.6 M in hexane) was added to the solution of **4** (2.40 g, 9.72 mmol) in THF (5 mL) at −78 ºC, and stirred for 15 min. After DMF (1.50 g, 0.75 mL, 9.72 mmol) was added and stirred for 20 min. Then, the solution was allowed to room temperature and stirred for 1 h. An aqueous saturated solution of NH_4Cl (5 mL) was added and the organic layer was extracted with diethyl ether (50 mL). The organic extracts were dried over Na_2SO_4, and the solvent was removed in the rotatory evaporator. The resulting residue was purified by column chromatography (silica gel 60-120, 1/3 (v/v) CH_2Cl_2/petroleum ether) to give a yellow oil (1.69 g). Yield: 89%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.04 (s, 1H), 7.64 (d, J = 5.1 Hz, 1H), 7.03 (d, J = 5.1 Hz, 1H), 2.96 (t, J = 7.5 Hz, 2H), 1.67-1.43 (m, 3H), 1.30-1.11 (m, 5H), 0.89 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.76; 152.44; 137.35; 134.04; 130.4; 31.28; 31.12; 28.56; 28.34; 22.12; 13.11.

Device Fabrication

FTO (F:SnO_2) glass (8 Ω/cm^2, 2.3mm thickness) was cleaned in a detergent solution in an ultrasonic bath for 20 min, followed by cleaning in DI water and ethanol for 10 min each, then dried using nitrogen. A transparent nanocrystalline layer on the FTO glass plate was prepared by screen printing of TiO_2 anatase particle (size ~20 nm) paste (T20/SP; Solaronix). This was gradually heated to 500 °C at a heating rate of ~10 °C/min and sintered at this temperature for 30 min. The thickness of the transparent layer was

measured by using an Alpha step surface profilometer and scanning electron microscopy (SEM) cross section. Then, a reflecting scattering layer containing ~ 400 nm sized TiO_2 anatase particles (Ti-Nanoxide R/SP; Solaronix) was also prepared by screen printing, followed by drying at room temperature for 10 min, and then gradually heated to 500 °C at a heating rate of ~10 °C/min and annealed at this temperature for 30 min. The resulting layer was composed of 12 μm thickness of transparent layer and 5 μm thickness of scattering layer. Both layers were treated by 40 mM $TiCl_4$ at 70 °C for 30 min and rinsed with water and ethanol and finally sintered at 500 °C for 30 min.

After cooling to 80°C the sintered electrodes were immediately immersed into the dyes (SY-04 and SY-05) synthesized in this work (0.3mM in ethanol) and kept at room temperature for 24 h. For comparison, the same electrode was also immersed into standard N3 dye with similar concentrations. The dye-adsorbed TiO_2 electrode was washed in ethanol, and dried with nitrogen blowing.

For the electrolyte injection, two holes were prepared on another FTO glass plate and cleaned in a detergent solution in an ultrasonic bath for 20 min, followed by cleaning in DI water and ethanol for 10 min each, then dried using nitrogen. Counter electrode was prepared by dropping transparent platinum catalyst (Platisol, Solaronix) on the FTO glass plate with two holes and heated at 400 °C for 5 min. A 60 μm thick hot melt ionomer film (Surlyn, SX1170-60 from Solaronix) was sandwiched between the TiO_2 working electrode and Pt counter electrode by heating at 110°C for a few seconds. The space between the electrodes was filled with liquid electrolyte consisting of 0.6M 1-butyl-3-methyl imidazolium iodide, 0.03M I_2, 0.1M guanidinium thiocyanate and 0.5M 4-tertbutylpyridine in a solvent mixture of acetonitrile and valeronitrile (volume ratio,

85:15). After the electrolyte injection, the holes were sealed with Surlyn and a thin cover glass.

References.

1. C. Ringenbach, A. De Nicola, R. Ziessel *J. Org. Chem.* 2003, **68***,* 4708.
2. S. Gould, G.F. Strouse, T.J. Meyer, Sullivan, B.P. *Inorg. Chem.* 1991, **30**, 2942.
3 F.Wang, R. D. Rauh, T. L Rose, *J. Am. Chem. Soc.* **1997**, *119*, 11106.

Table S1. DFT molecular orbital energies of **SY-04** and **SY-05**.[a]

SY-04			SY-05		
MO	Gas –E(eV)	Solvent -E(eV)	MO	Gas –E(eV)	Solvent -E(eV)
287	6.23	6.69	239	6.26	6.80
288	6.01	6.26	240	6.04	6.26
289	5.90	6.01	241	5.96	6.01
290	4.95	5.96	242	4.98	5.96
291	4.79	5.61	243	4.82	5.61
292	4.73	5.50	244	4.76	5.50
293	**4.54**	**5.25**	**245**	**4.54**	**5.25**
294	**2.86**	**2.83**	**246**	**2.86**	**2.80**
295	2.64	2.53	247	2.69	2.50
296	2.34	2.23	248	2.39	2.20
297	2.29	2.15	249	2.29	2.15
298	2.01	1.90	250	2.04	1.88
299	1.90	1.77	251	1.90	1.74
300	0.76	0.57	252	0.87	0.60

[a]The values written in boldface are used for the HOMO (293, 245) and LUMO (294, 246).

Table S2. TDDFT excitation energies (eV) and oscillator strengths (f) for the optical transition with f>0.01 of **SY-04** in the gas phase.

State	Composition	E(eV)	f
1	13%(291→294); 16%(292→294); 60%(293→294); 11%(293→295)	1.086	0.017
3	25%(291→294); 15%(292→295); 60%(293→295)	1.353	0.037
4	45%(291→294); 36%(292→294); 19%(293→297)	1.439	0.030
5	33%(290→294); 67%(292→295)	1.599	0.031
6	80%(291→295); 20%(292→295)	1.616	0.017
7	66%(290→294); 34%(291→295)	1.634	0.011
8	15%(290→295); 85%(293→296)	1.756	0.053
9	12%(290→294); 46%(290→295); 43%(293→297)	1.844	0.054
10	67%(290→295); 16%(292→295); 17%(293→298)	1.902	0.093
11	72%(292→297); 28%(293→298)	1.936	0.018
14	41%(292→296); 29%(292→297); 30%(293→298)	1.989	0.037
15	43%(291→296); 30%(291→297); 14%(292→296); 13%(292→297)	2.043	0.016
18	82%(290→296); 18%(293→299)	2.210	0.024
20	32%(290→296); 68%(290→297)	2.256	0.035
25	10%(285→294); 33%(287→294); 57%(288→294)	2.531	0.010
27	22%(286→295); 17%(287→294); 61%(289→295)	2.739	0.211
28	42%(287→294); 14%(287→295); 34%(288→295); 10%(288→297)	2.794	0.254
30	16%(286→294); 10%(288→294); 40%(288→295); 17%(289→295); 17%(289→296)	2.973	0.044
31	14%(285→294); 56%(286→294); 12%(288→294); 18%(288→297)	3.071	0.033
32	12%(285→297); 17%(286→294); 17%(286→297); 54%(289→297)	3.111	0.010
33	29%(285→294); 13%(288→296); 31%(289→296); 26%(289→297)	3.154	0.290
34	67%(285→294); 17%(286→295); 16%(288→296)	3.184	0.154
35	78%(286→295); 22%(288→295)	3.223	0.178
36	11%(286→294); 13%(287→296); 64%(288→296); 13%(293→300)	3.238	0.195
37	22%(286→297); 78%(287→297)	3.315	0.063
38	20%(287→297); 51%(289→298); 29%(293→300)	3.343	0.106
39	100%(293→300)	3.353	0.032
40	53%(287→296); 47%(287→297)	3.374	0.014

Table S3. TDDFT excitation energies (eV) and oscillator strengths (f) for the optical transition with f>0.01 of **SY-05** in the gas phase.

State	Composition	E(eV)	f
1	81%(245→246); 19%(245→247)	1.090	0.018
3	85%(245→247); 15%(245→248)	1.330	0.034
4	32%(243→246); 7%(243→247); 27%(244→246); 9%(245→246); 11%(245→247); 14%(245→249)	1.437	0.032
5	18%(242→246); 58%(244→247); 13%(245→247); 10%(245→248)	1.567	0.022
6	100%(243→247)	1.592	0.026
8	19%(242→247); 81%(245→248)	1.720	0.045
9	11%(242→246); 53%(242→247); 36%(245→249)	1.830	0.063
10	17%(242→246); 25%(245→248); 58%(245→249)	1.879	0.094
11	100%(244→248)	1.925	0.028
15	39%(243→248); 37%(243→249); 13%(244→248); 11%(244→249)	2.001	0.025
18	82%(242→248); 18%(245→251)	2.177	0.020
20	16%(242→248); 84%(242→249)	2.239	0.035
27	17%(238→247); 10%(239→246); 24%(240→247); 49%(241→247)	2.728	0.144
28	34%(239→246); 19%(239→247); 28%(240→246); 9%(240→249); 11%(241→247)	2.793	0.297
30	9%(239→246); 28%(239→247); 28%(240→247); 10%(240→248); 12%(240→249); 14%(241→248)	2.966	0.033
31	44%(238→246); 11%(238→249); 19%(240→249); 26%(241→249)	3.116	0.027
32	20%(238→249); 80%(241→249)	3.137	0.023
33	60%(241→248); 40%(241→249)	3.145	0.245
34	13%(238→248); 12%(239→249); 54%(240→248); 20%(241→248)	3.205	0.274
35	52%(237→246); 27%(240→248); 9%(240→249); 12%(241→246)	3.233	0.033
36	85%(238→247); 15%(245→252)	3.256	0.155
37	22%(240→248); 78%(245→252)	3.276	0.012
38	19%(237→246); 81%(239→248)	3.325	0.026
39	26%(239→248); 27%(239→249); 9%(240→248); 13%(240→249); 25%(241→250)	3.348	0.049
40	100%(241→250)	3.354	0.122

Table S4. Photovoltaic performance of DSCs prepared by three sensitizers under AM 1.5 light illumination (100 mW cm^{-2}) with a mask.

Dyes	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η(%)	Active Area/cm^2
SY-04	12.9	0.710	0.708	6.5	0.468
SY-05	11.4	0.725	0.718	6.0	0.478
N3	11.2	0.683	0.670	5.1	0.462

Table S5. Photovoltaic performance of DSCs prepared by different sensitizers and different TiO_2 layer thickness under AM 1.5 light illumination (100 mW cm^{-2}). The active areas of the cells were 0.250 cm^2 without a mask. Also, a reflecting-scattering layer was not used.

Dyes	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)	Thickness (μm)
SY-04	14.2	0.733	0.681	7.1	12
SY-04	17.7	0.654	0.606	7.0	8
SY-04	16.8	0.669	0.615	6.9	6
SY-04	10.5	0.666	0.707	4.9	4
SY-05	13.9	0.745	0.680	7.0	12
SY-05	17.3	0.664	0.591	6.8	8
SY-05	16.5	0.682	0.598	6.7	6
SY-05	12.5	0.628	0.661	5.2	4
N3	12.5	0.605	0.686	5.2	12
N3	11.0	0.629	0.637	4.4	8
N3	11.2	0.570	0.580	3.7	6
N3	9.8	0.545	0.580	3.1	4

Table. S6. Photovoltaic performance of the DSCs prepared by three sensitizers with 1.0 x 10^{-4} concentration of under AM 1.5G light illumination (100 mW cm^{-2}). The active areas of the cells were 0.250 cm^2 without a mask. Also, a reflecting-scattering layer was not used.

Dyes	Concentration (mole)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)	Thickness (μm)
SY-04	1 x 10^{-4}	17.4	0.660	0.601	6.9	8
SY-05	1 x 10^{-4}	16.5	0.682	0.598	6.7	8
N3	1 x 10^{-4}	12.1	0.605	0.556	4.0	8

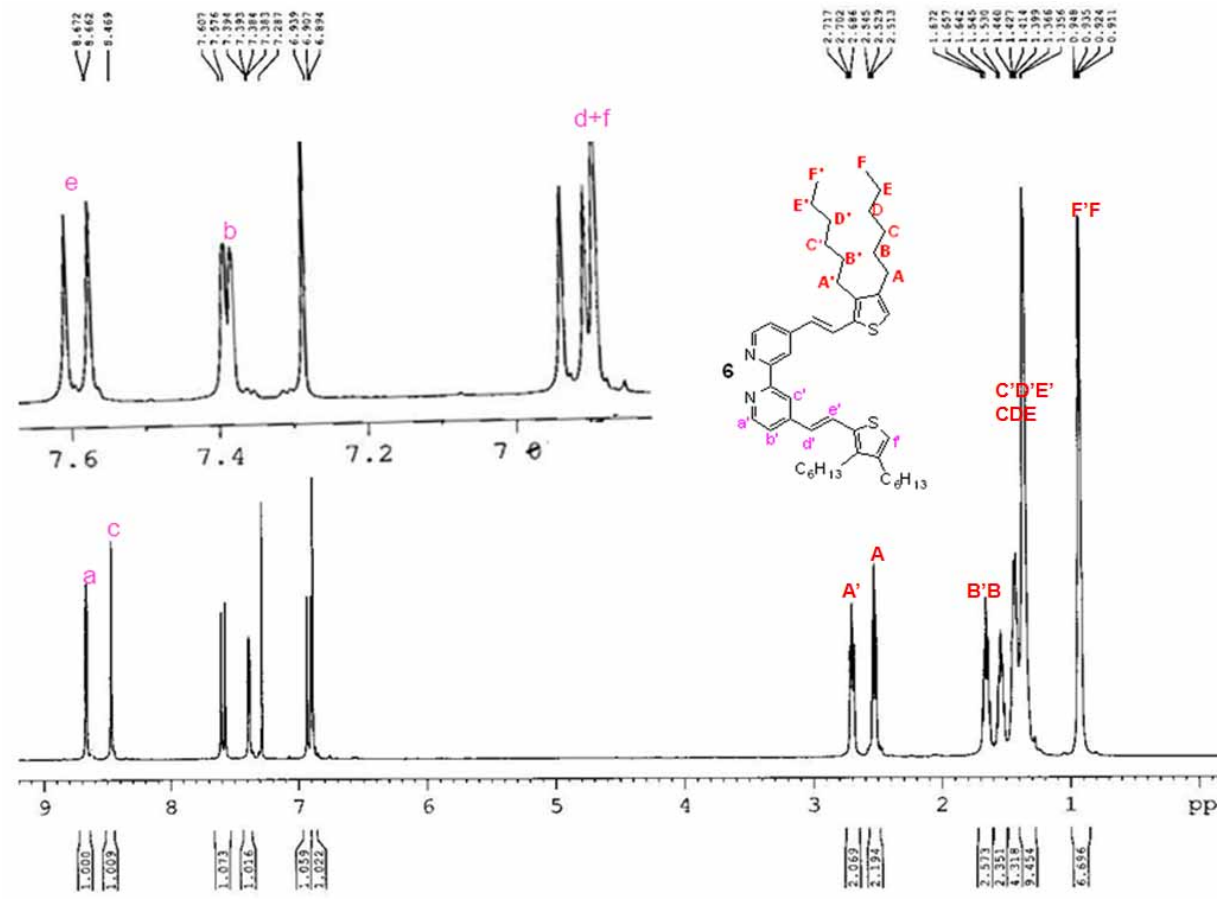

Figure S1(a). ^{1}H- NMR spectrum of ligand **6**.

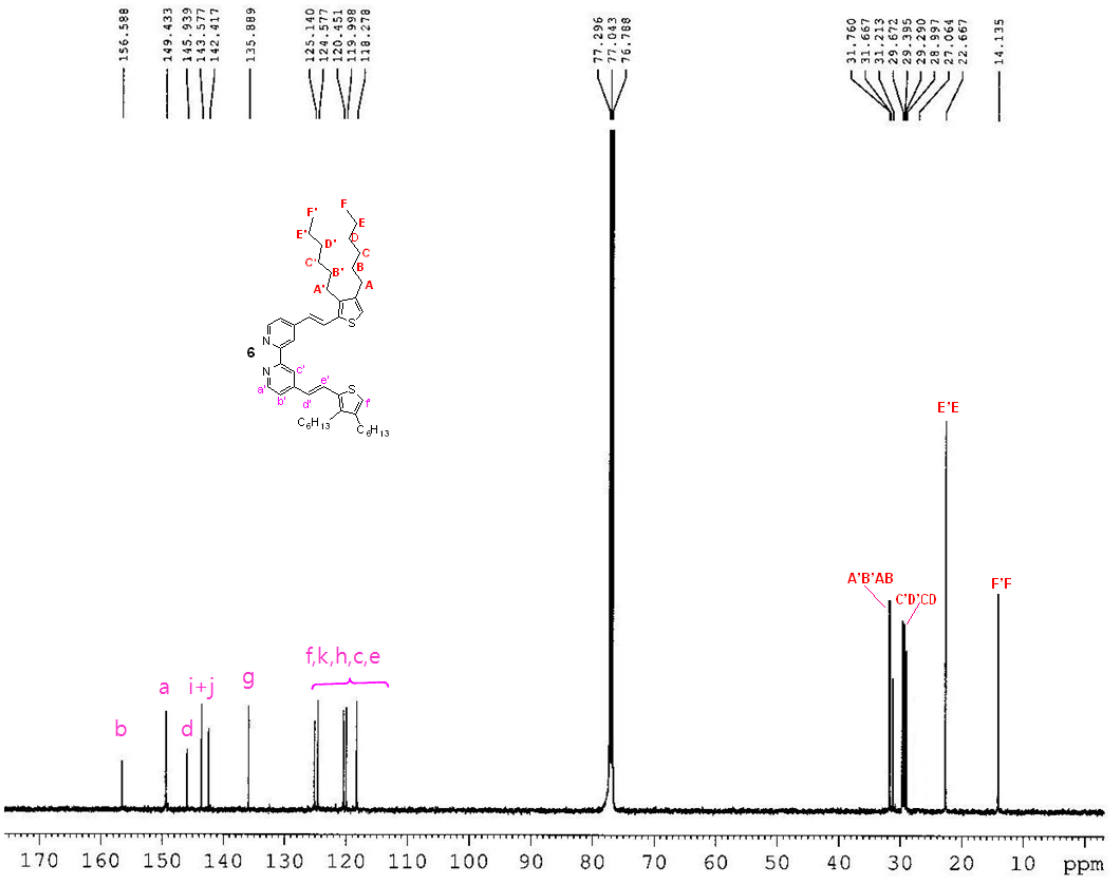

Figure S1 (b). ^{1}C- NMR spectrum of ligand **6**.

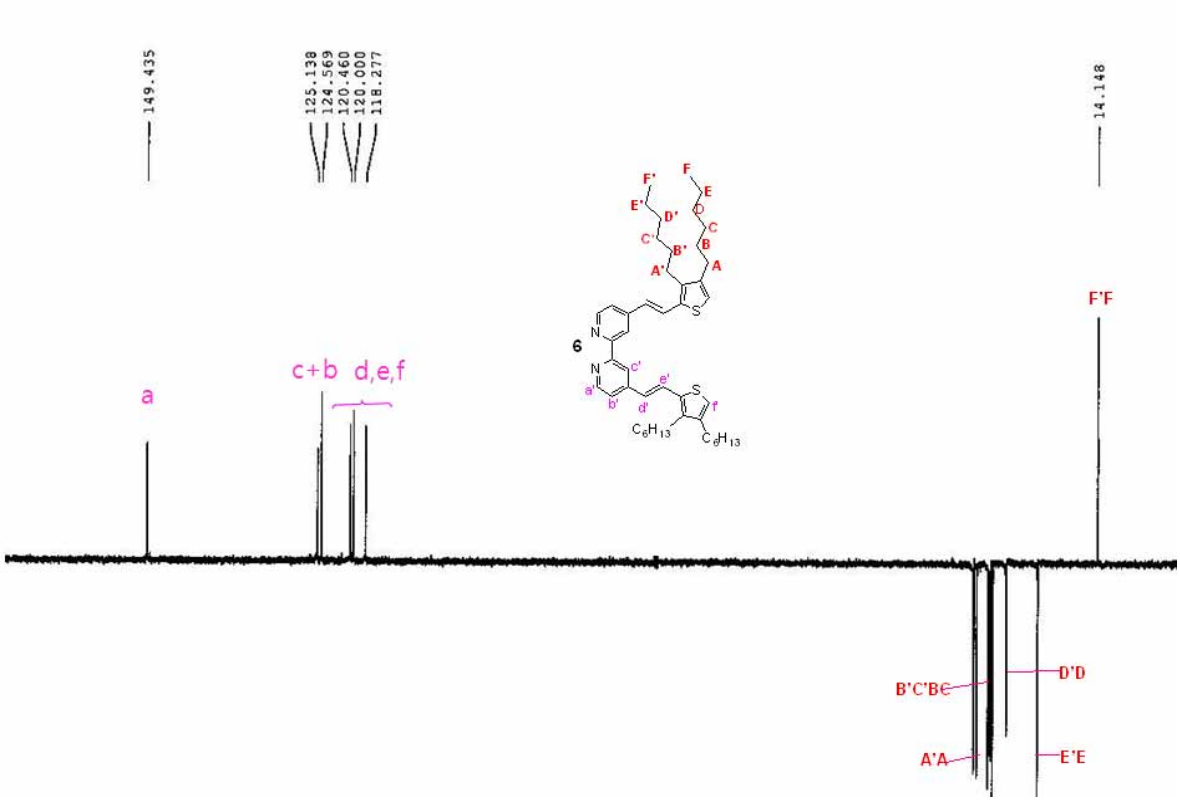

Figure S1(c). ^{13}C- DEPT135 spectrum of compound **6**.

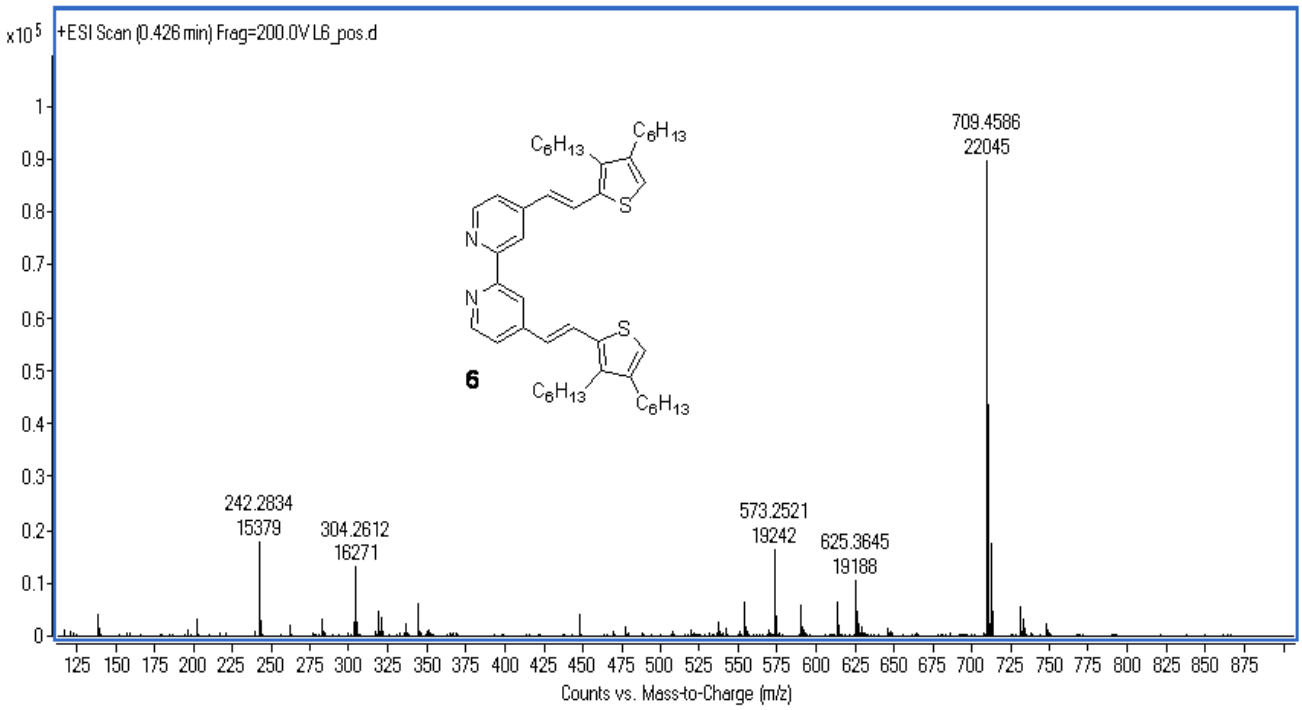

Figure S1(d). ESI mass spectrum of compound **6**.

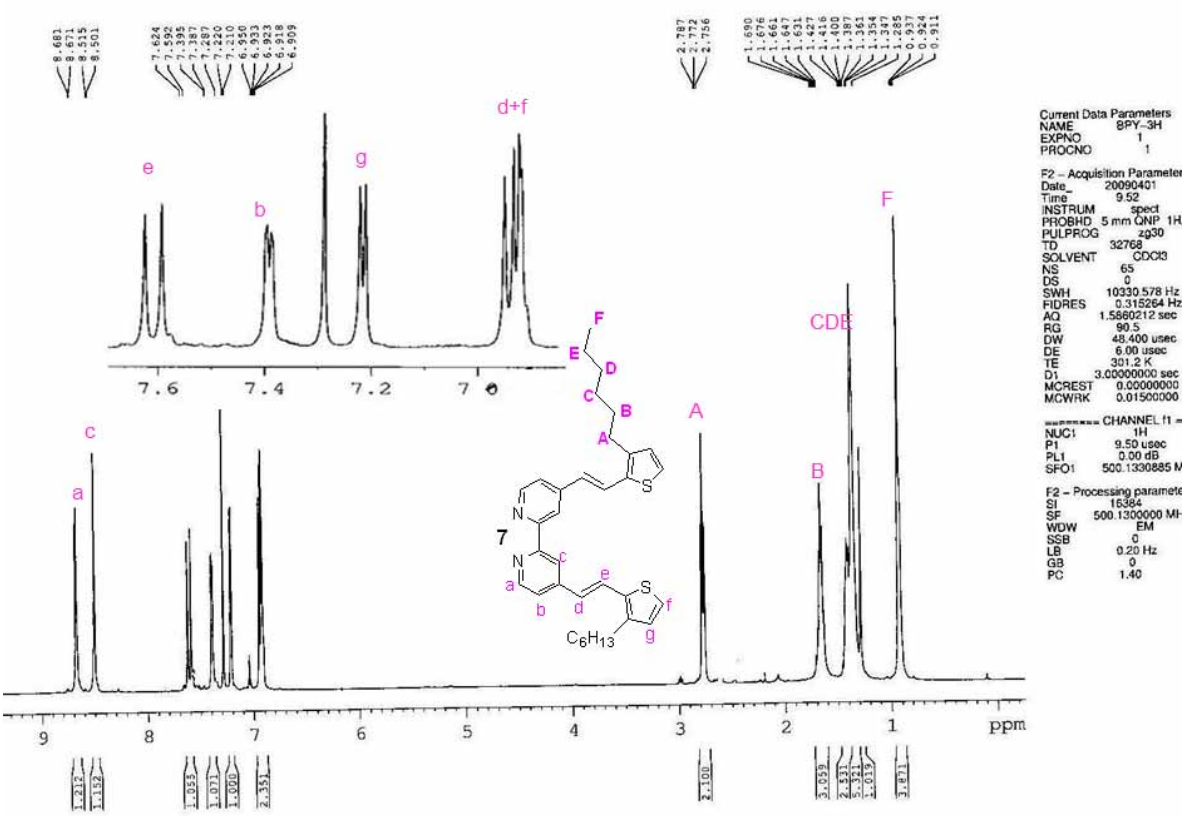

Figure S2(a). ^{1}H- NMR spectrum of ligand **7**.

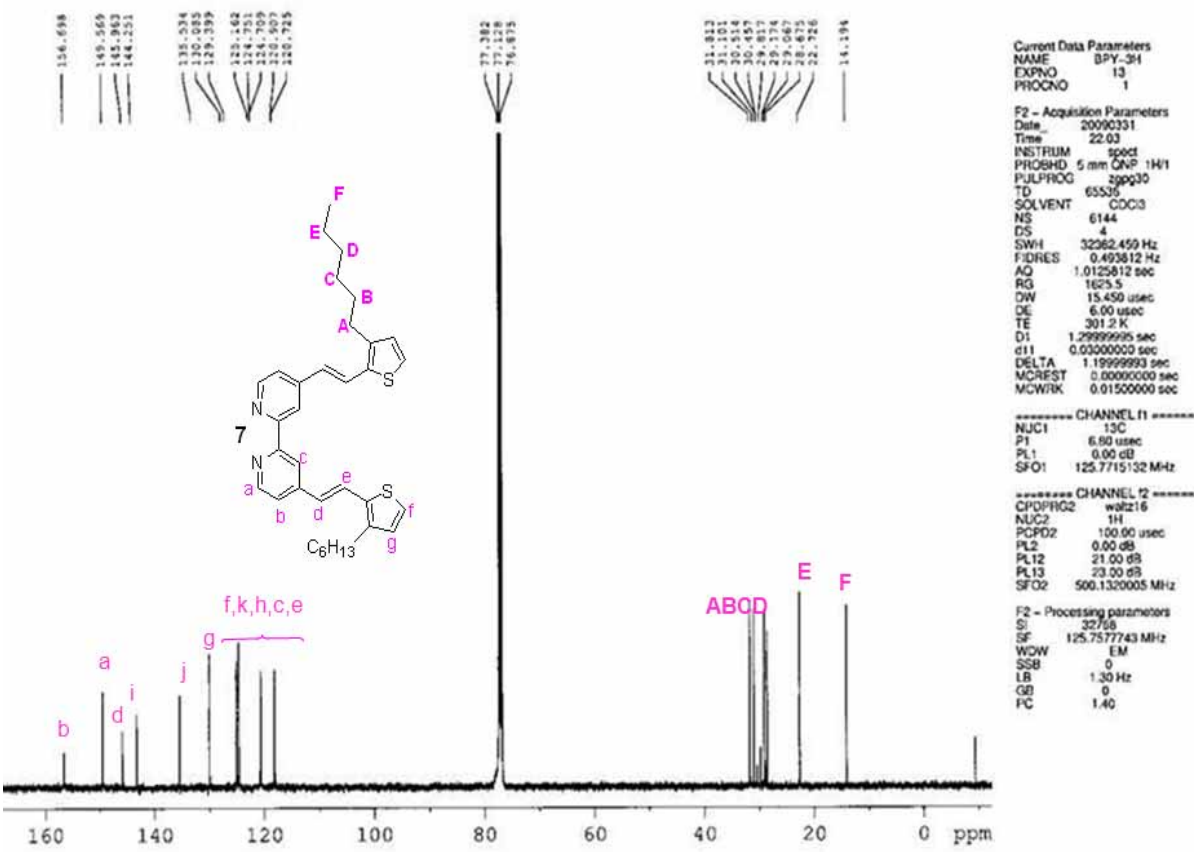

Figure S2(b). ^{13}C- NMR spectrum of ligand **7.**

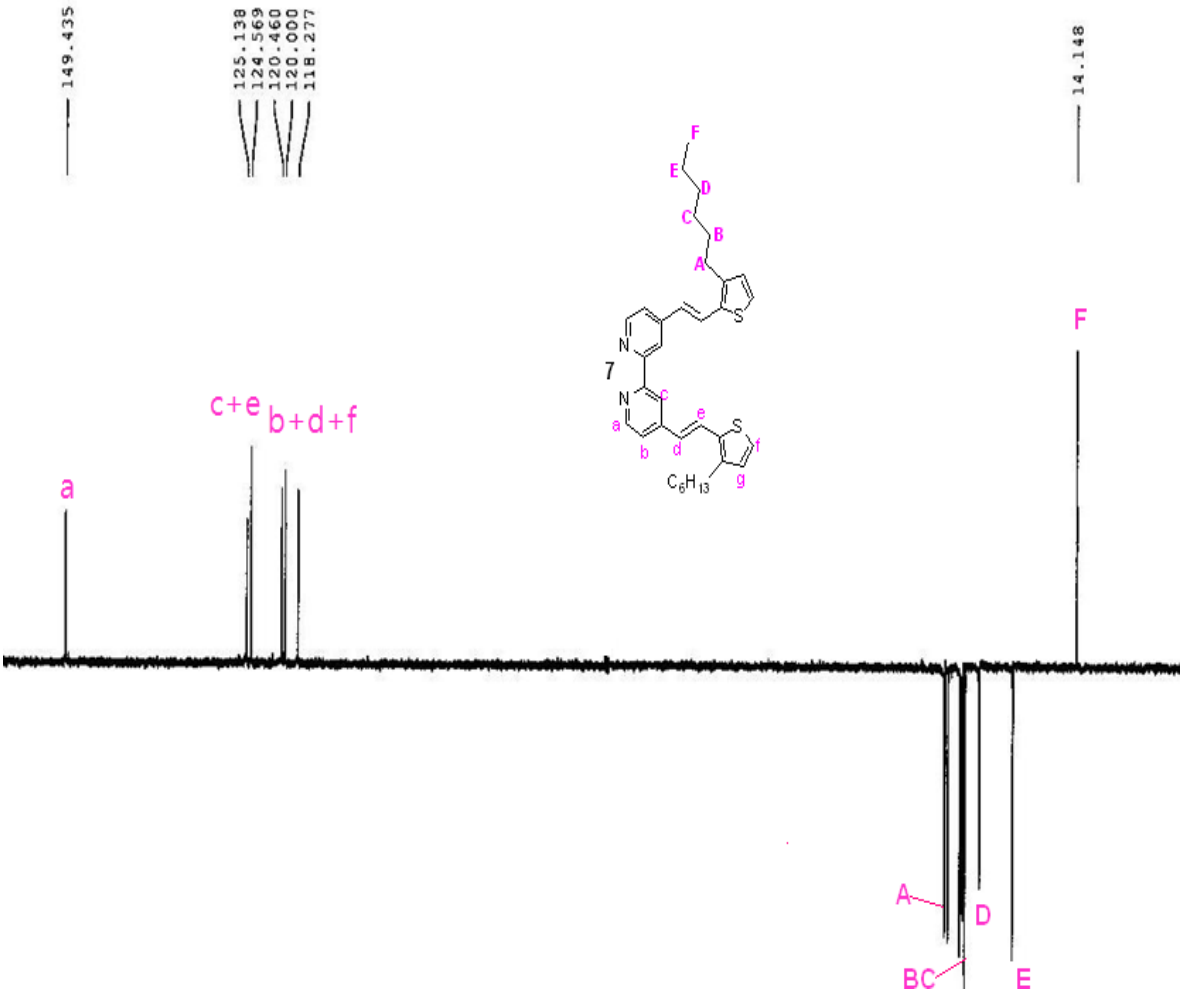

Figure S2(c). ^{13}C- DEPT135 spectrum of compound **7.**

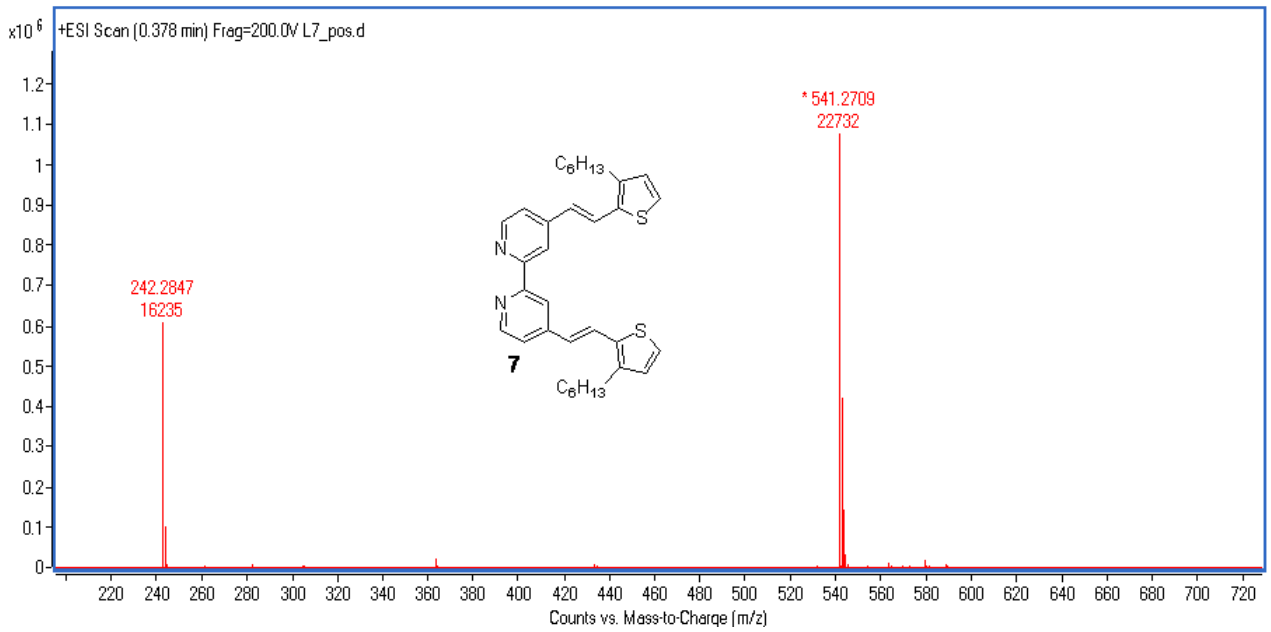

Figure S2(d). ESI mass spectrum of compound **7**.

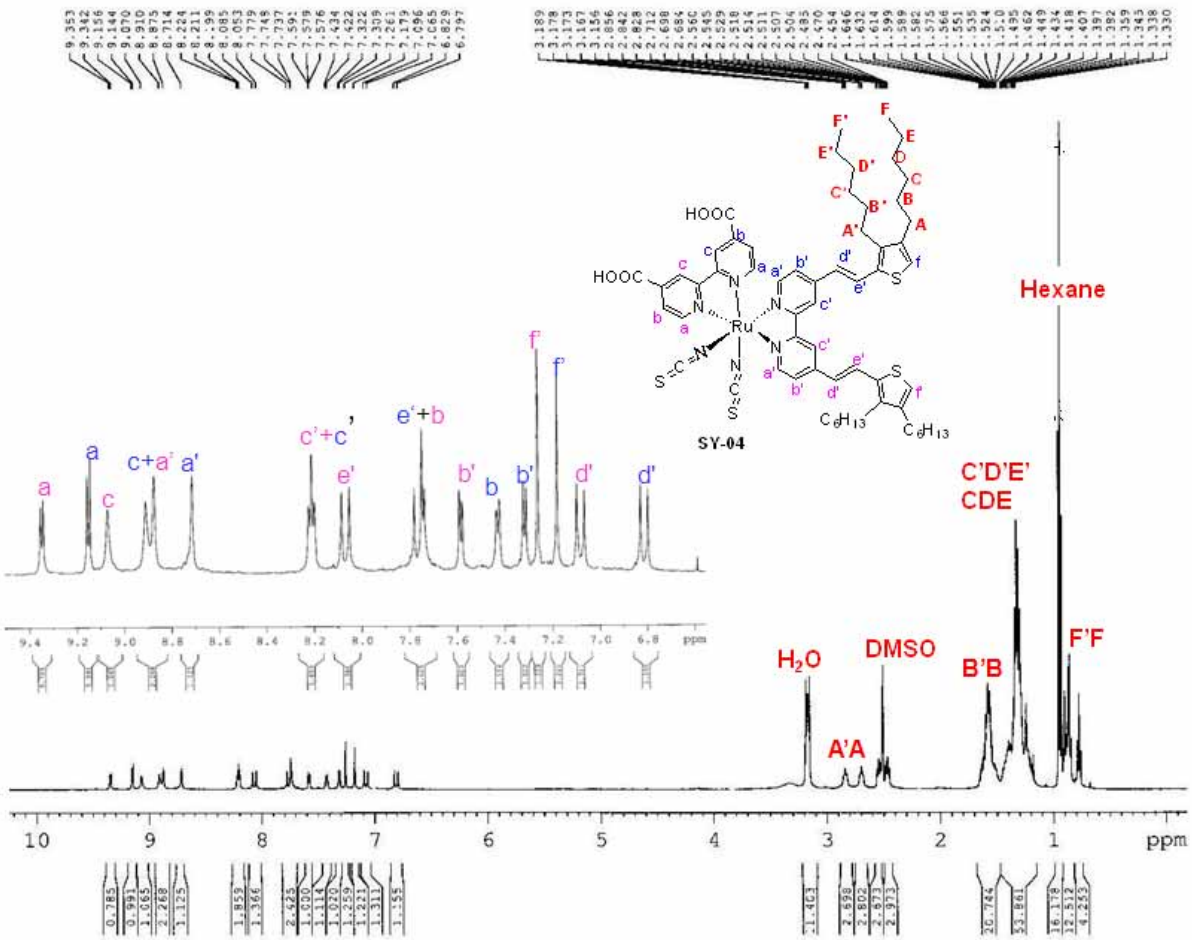

Figure S3 (a). ^{1}H–NMR Spectrum of **SY-04**.

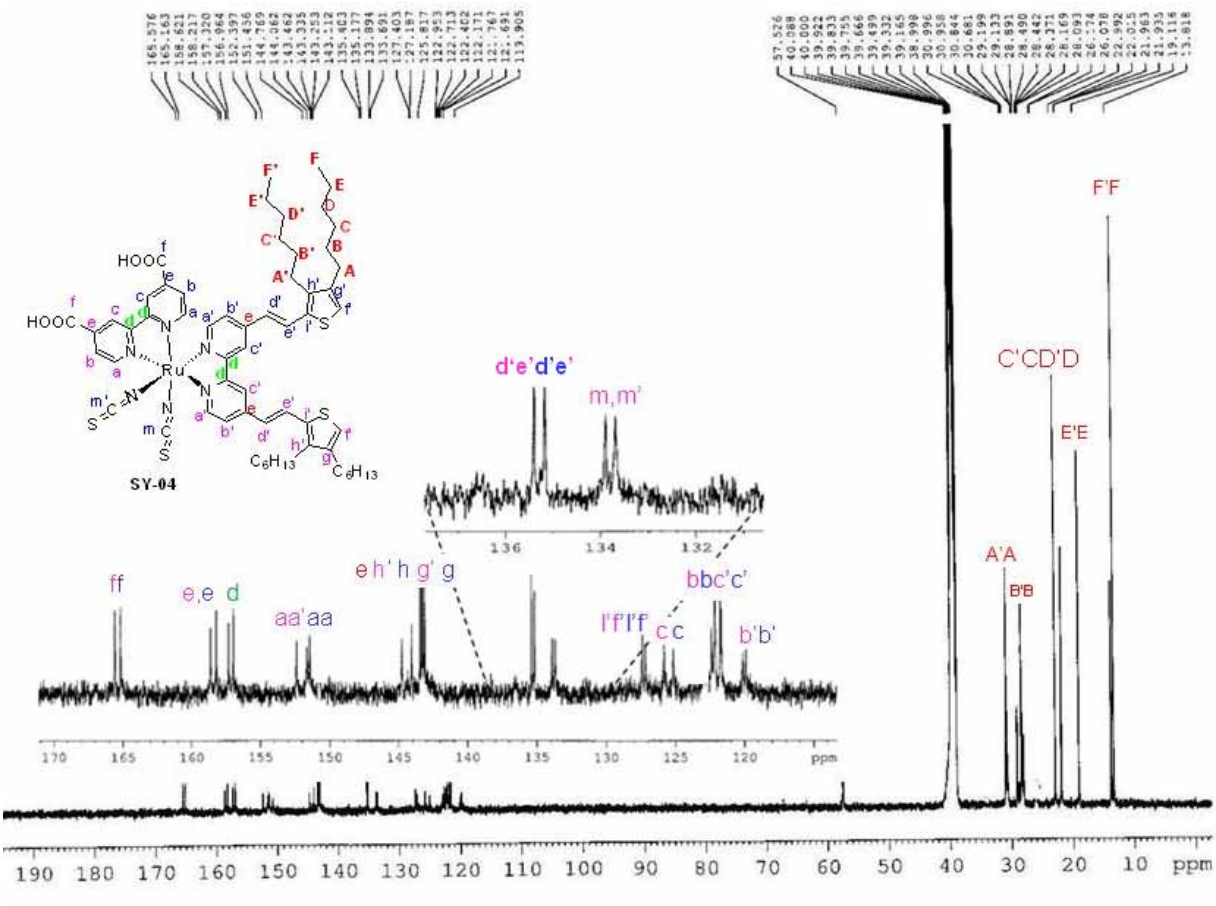

Figure S3 (b). ^{13}C –NMR Spectrum of **SY-04**.

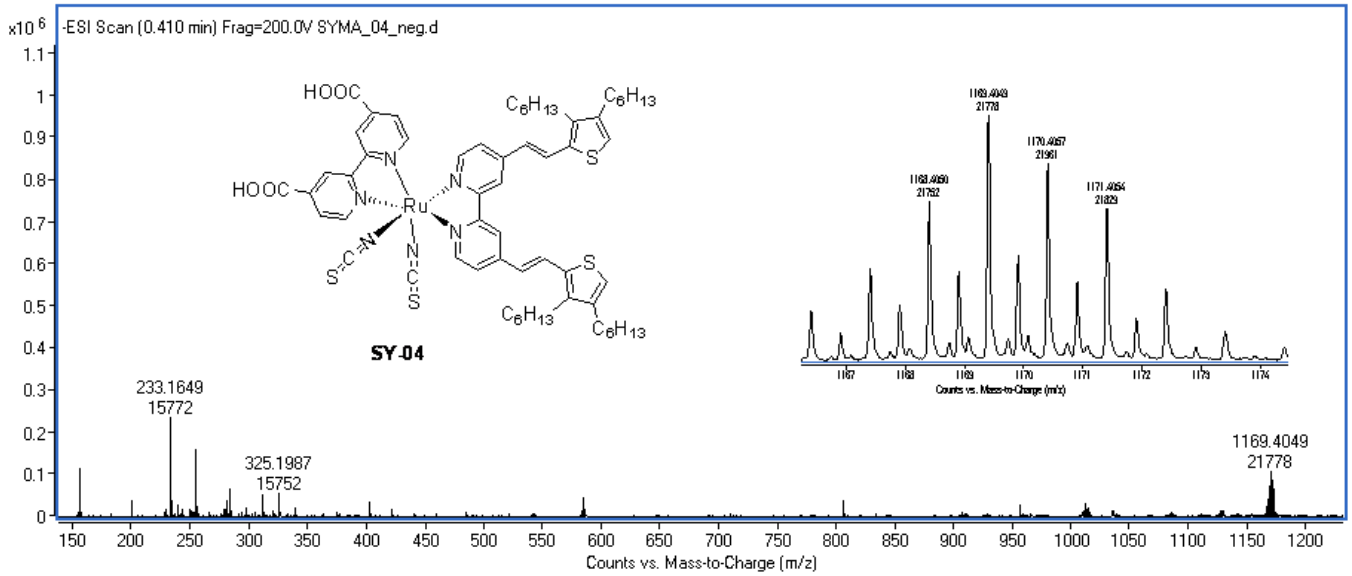

Figure S3(c). ESI mass spectrum of compound **SY-04**.

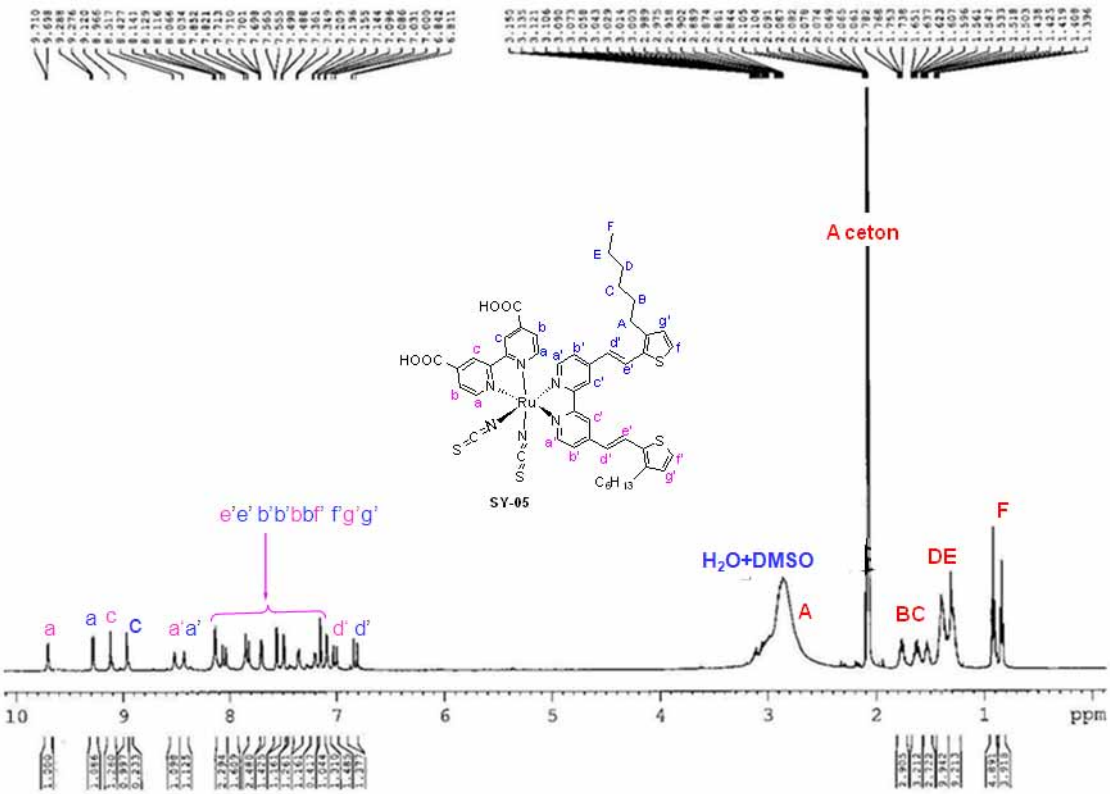

Figure S4 (a). ^{1}H –NMR Spectrum of **SY-05**.

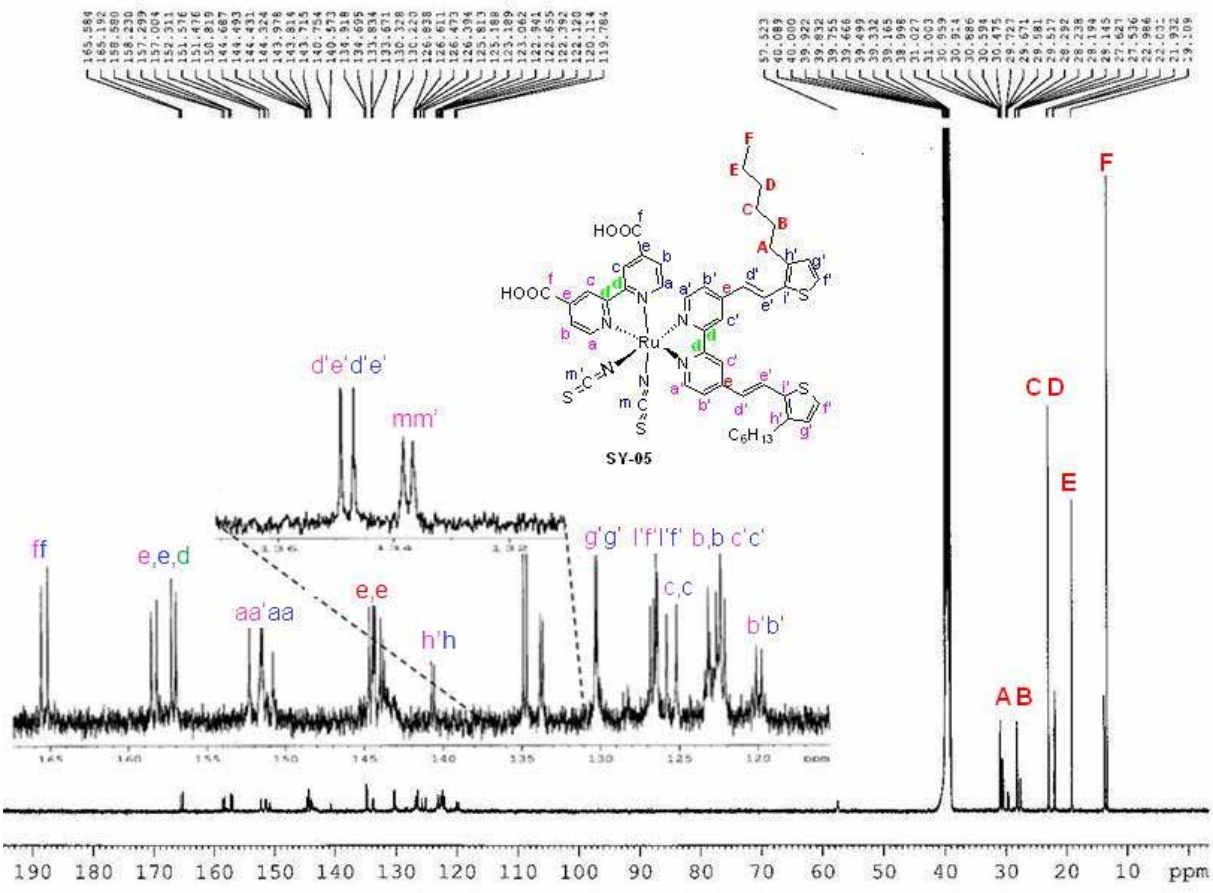

Figure S4 (b). ^{13}C- NMR spectra of **SY-05**.

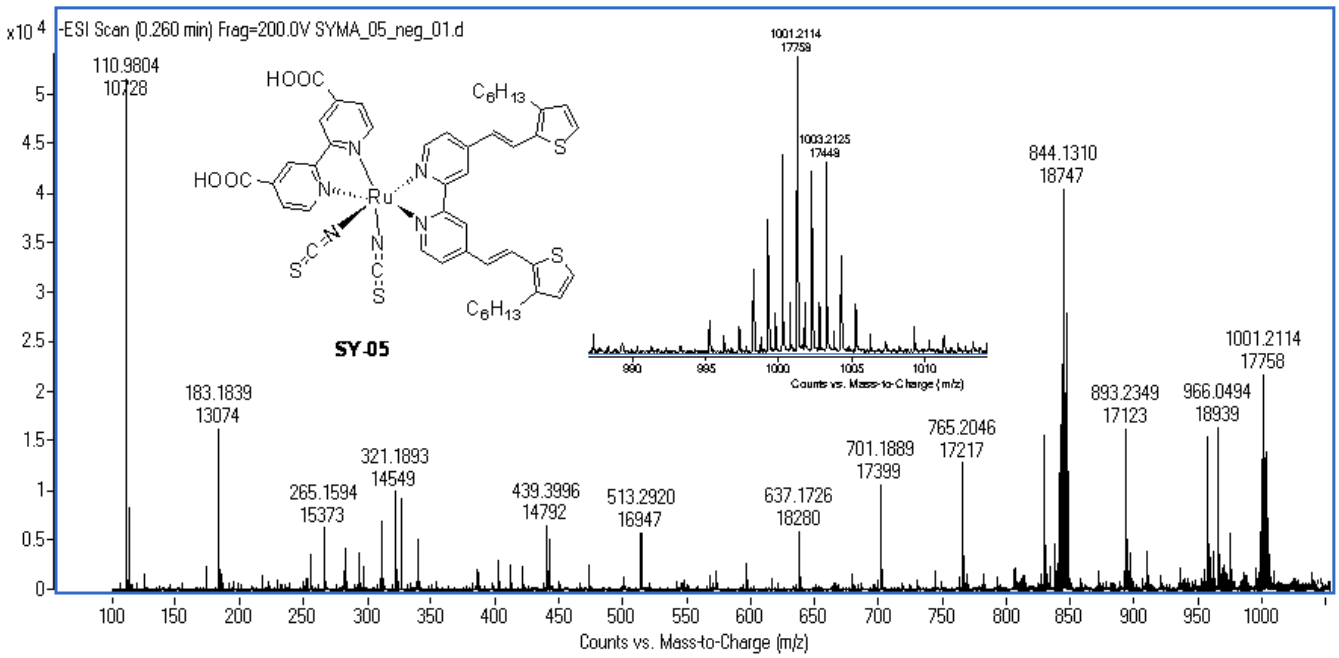

Figure S4(c). ESI mass spectrum of compound **SY-05**.

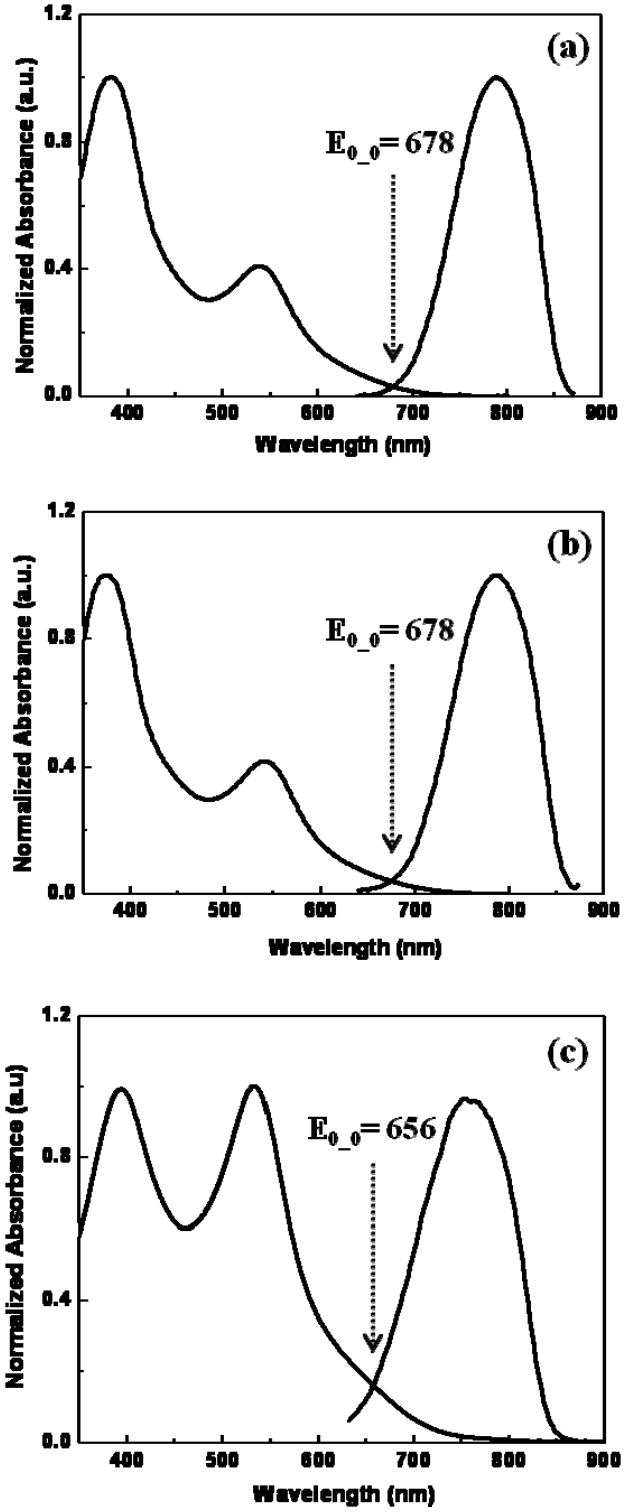

Figure S5. Absorption (left) and emission (right) spectra of **SY-04** (a), **SY-05** (b) and **N3** (c).

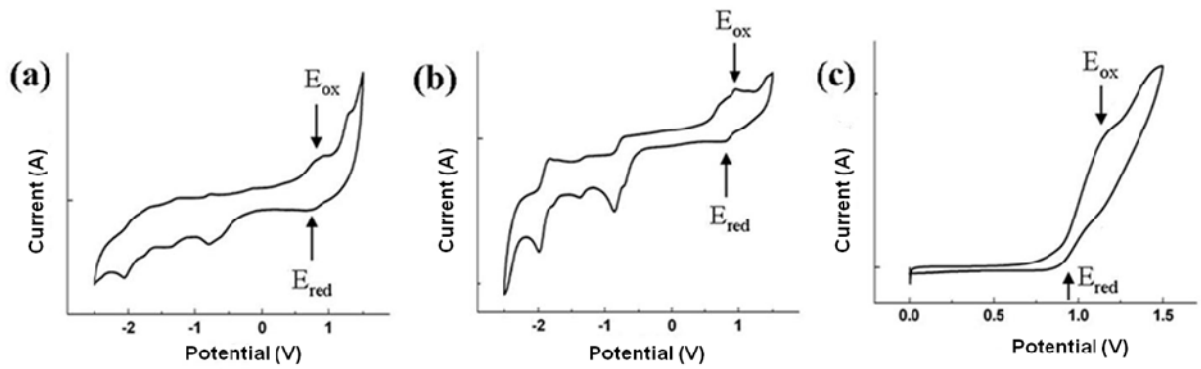

Figure S6. Cyclic voltammogram of **SY-04** (a), **SY-05** (b) and **N3** (c) with 0.1M (n-$C_4H_9)_4NPF_6$ in DMF solution (scan rate 100 mV s^{-1}).

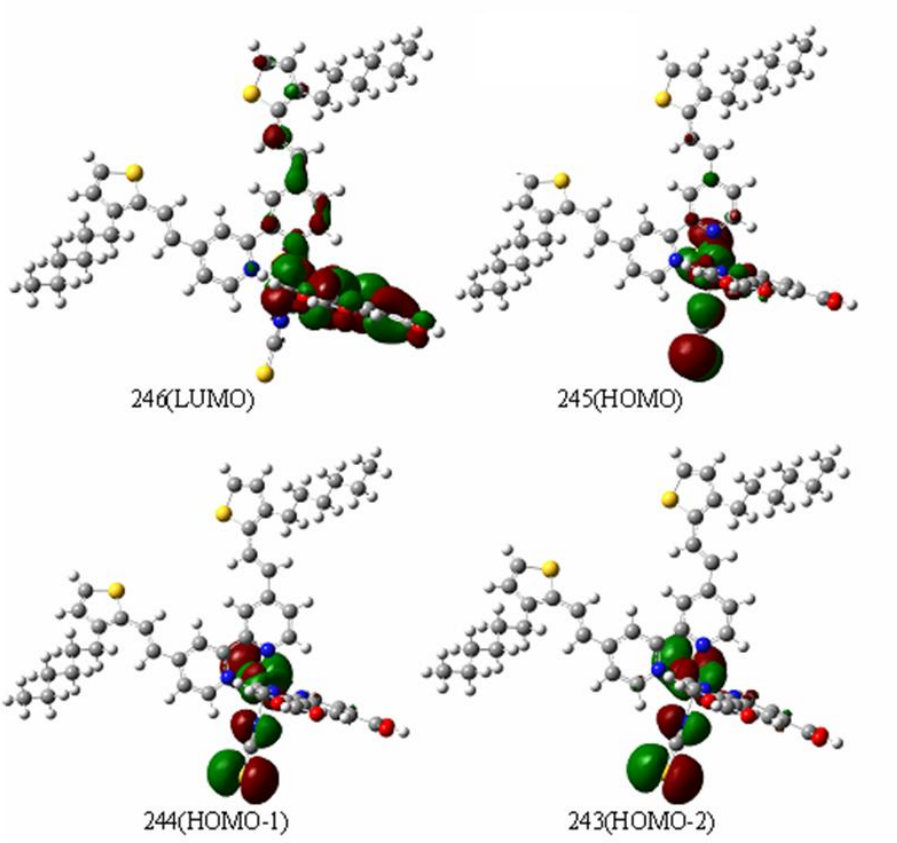

Figure S7. Isodensity surface plot (isodensity contour =0.02) of the **SY-05** molecular orbitals 246(LUMO), 245(HOMO), 244(HOMO-1) and 243(HOMO-2).

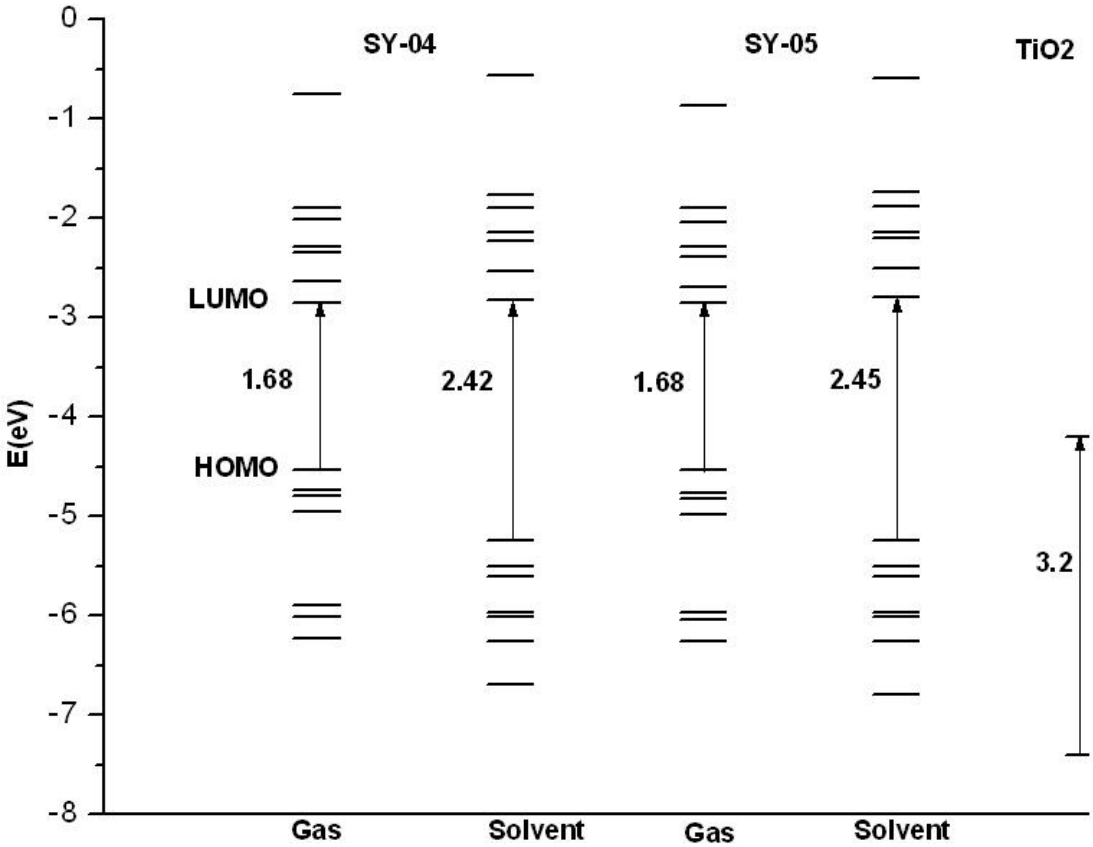

Figure S8. Energy level diagram of occupied and unoccupied frontier orbitals (HOMO and LUMO) of **SY-04**, **SY-05** and TiO_2.

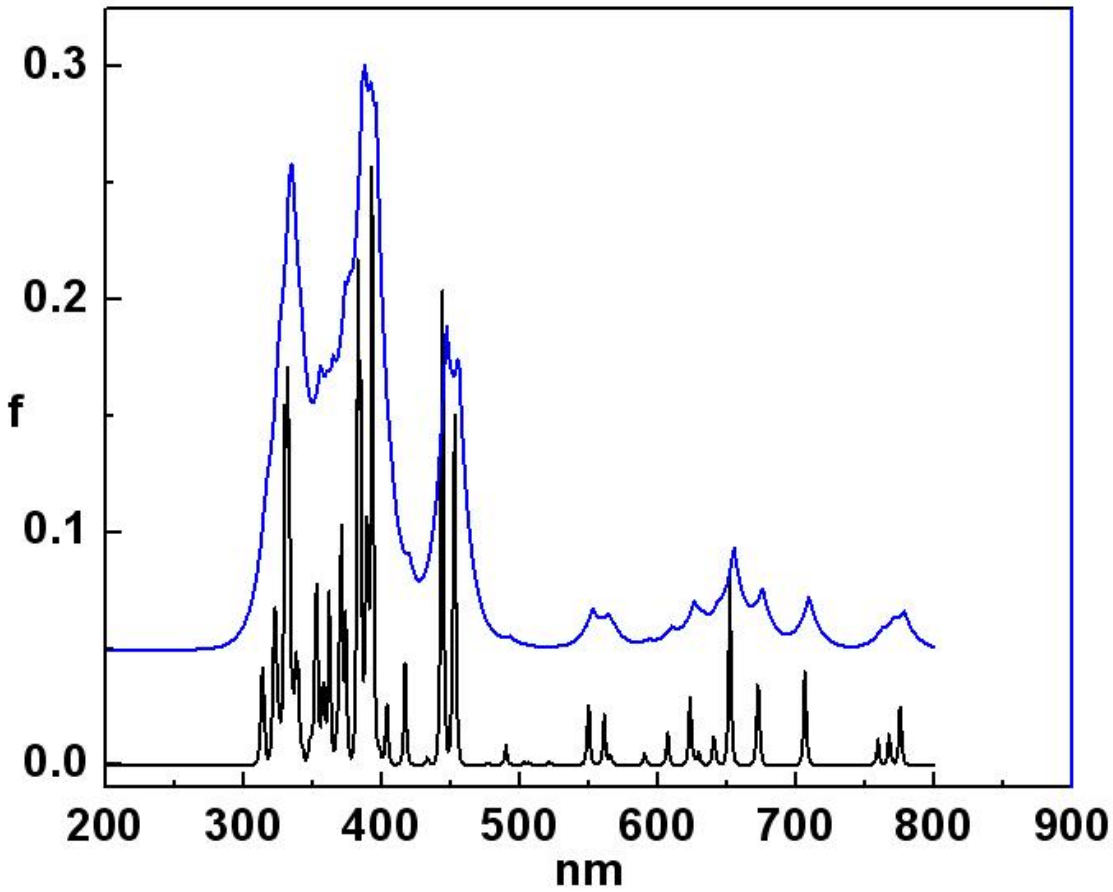

Figure S9. Computed absorption spectrum of **SY-04**: Oscillator strengths (f) vs. vertical excitation energy (The Gaussian smoothing is given in blue color).

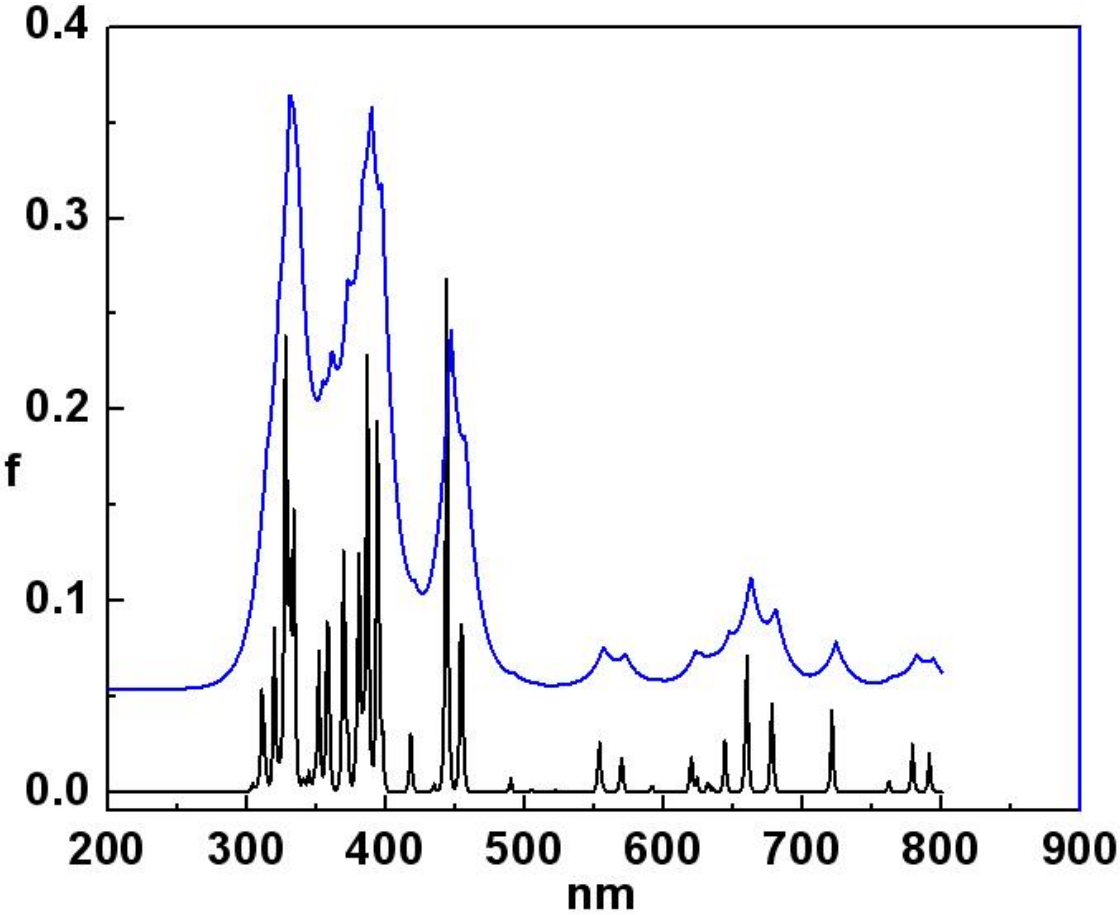

Figure S10. Computed absorption spectrum of **SY-05**: Oscillator strength (f) vs. vertical excitation energy (The Gaussian smoothing is given in blue color).

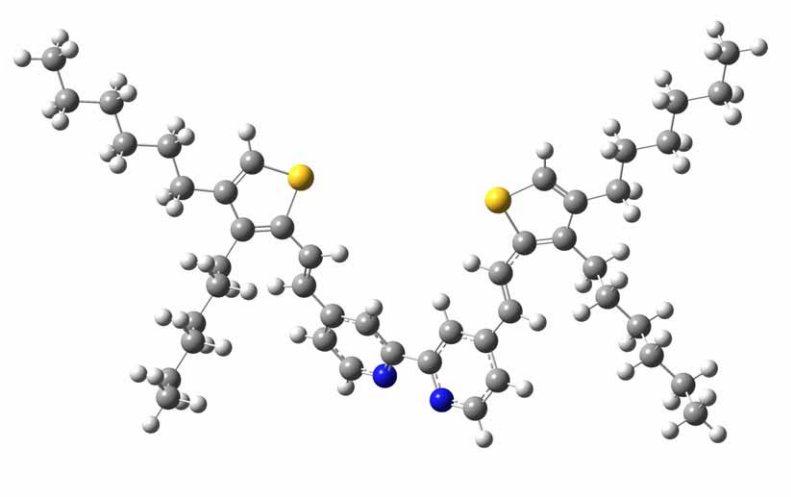

Figure S11. DFT optimized molecular structure of ligand **6.**

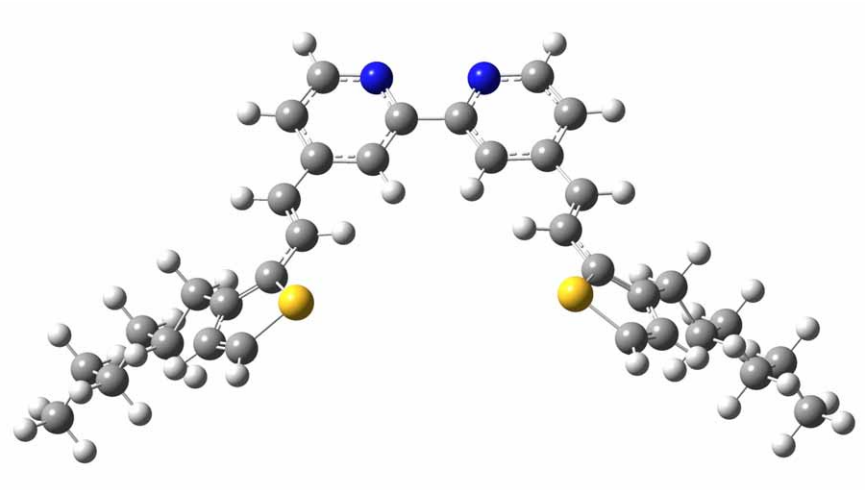

Figure S12. DFT optimized molecular structure of ligand **7.**

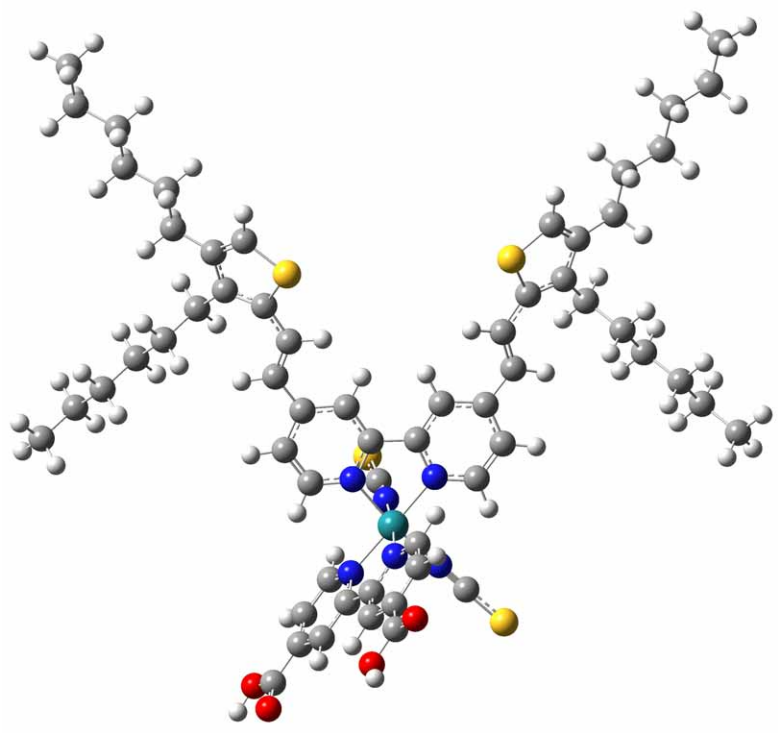

Figure S13. DFT optimized molecular structure of **SY-04.**

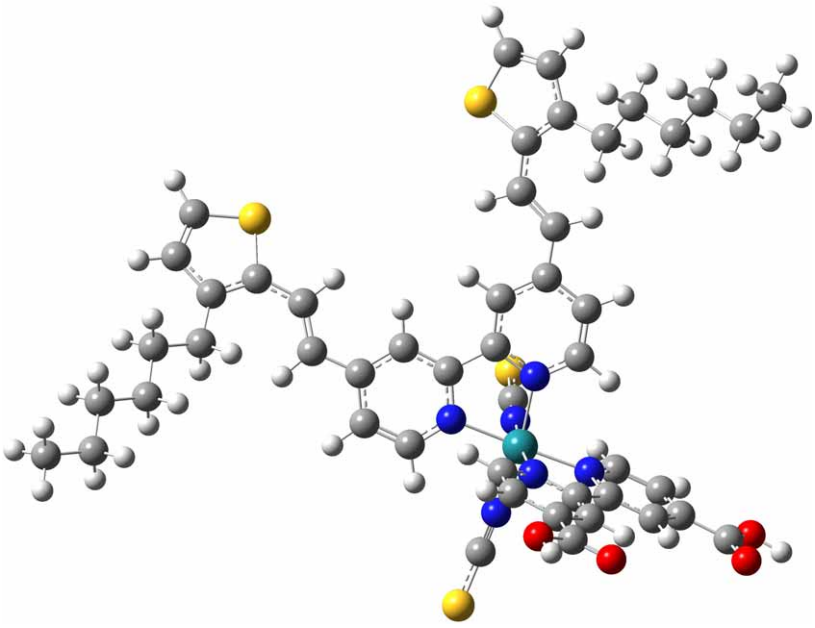

Figure S14. DFT optimized molecular structure of **SY-05**.

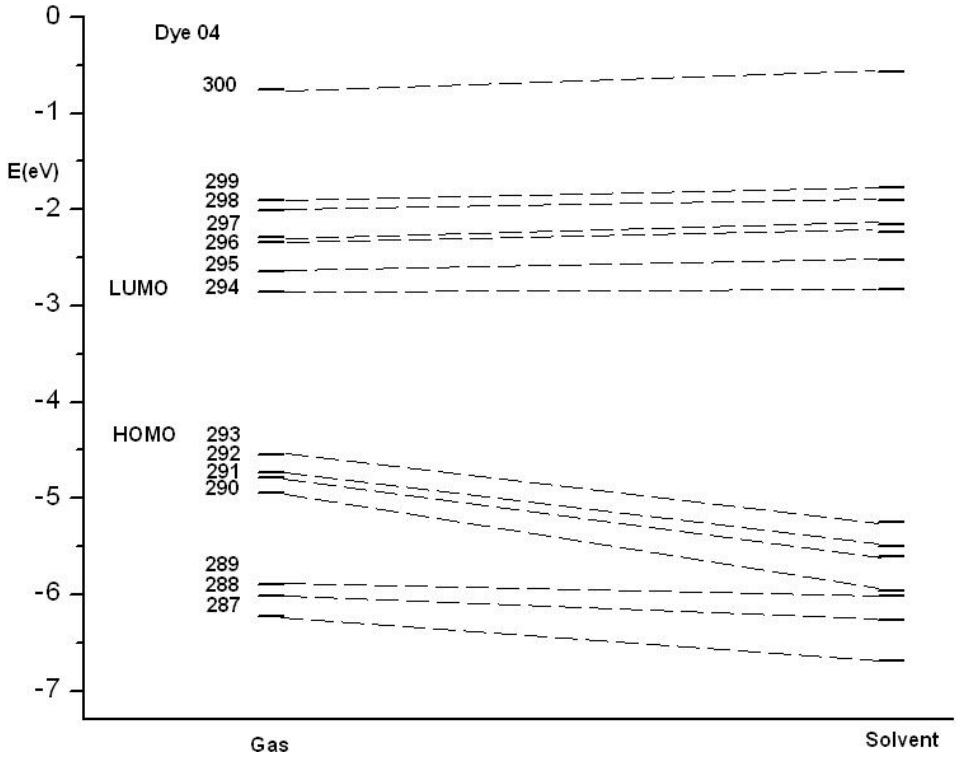

Figure S15. Calculated energy levels (eV) of **SY-04** in the gas phase and in solvent (ethanol).

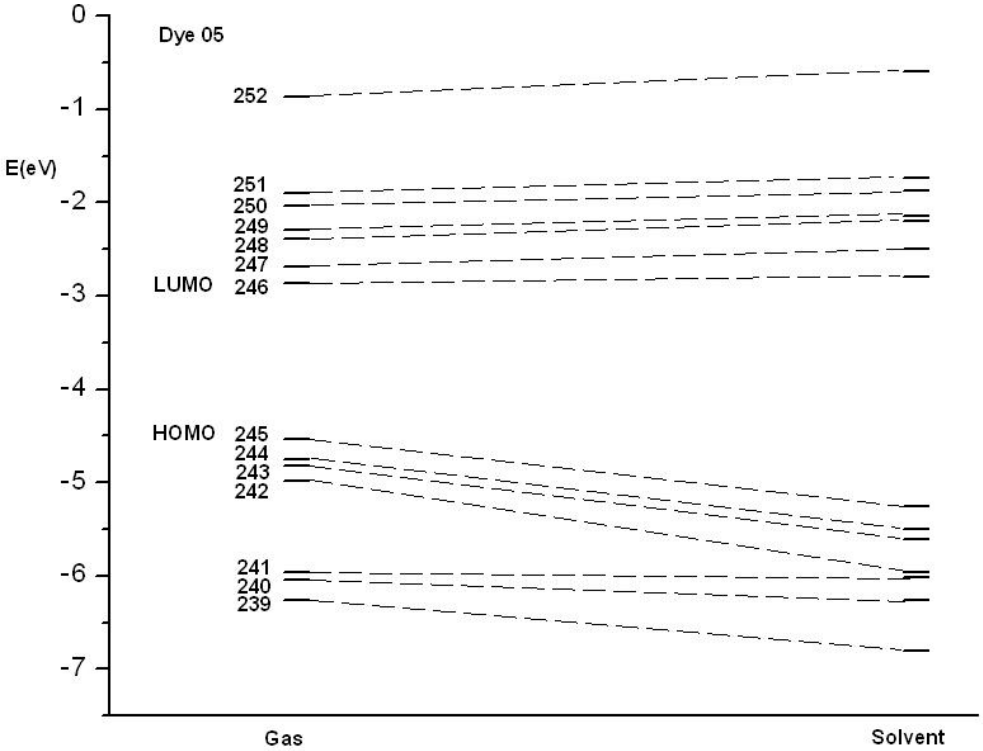

Figure S16. Calculated energy levels (eV) of **SY-05** in the gas phase and in solvent (ethanol).

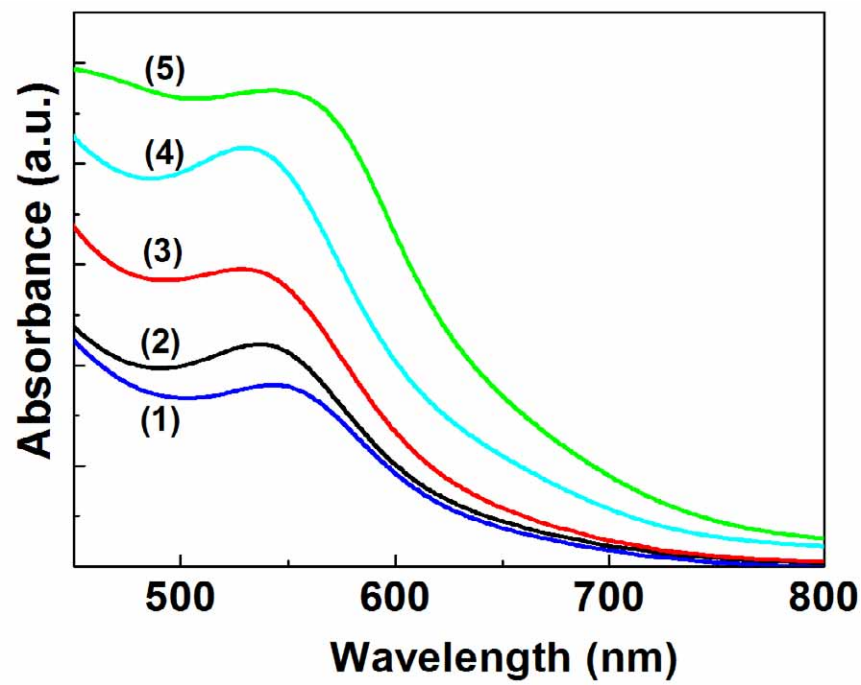

Figure S17. Absorption spectrum of **SY-04** adsorbed on various thickness of transparent nanocrystalline TiO_2 films: 4 μm (1), 6 μm (2), 8 μm (3), 12 μm (4), and 17 μm (5).