Supplementary Information

New phenothiazine-bridged dyes comprising both type-I and type-II photoinjections for DSSCs

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1. Synthesis procedures for the six new dyes.

General synthetic procedure for 2. A mixture of compound 1 (1.0 mmol), CB-$B(OH)_2$ (2.0 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and K_2CO_3 (2M, 1mL) in THF solution was heated to reflux under a N_2 atmosphere for about 18 h. Then, the solvent was removedunder vacuum and the residue was purified by column chromatography on silica gel using a 1:4 (v/v) mixture of Petroleum ether and CH_2Cl_2 as eluent to afford compound 2 as yellow solids, respectively.

General synthetic procedure for 3. A mixture of compound 2 (0.23 mmol), cyanoacetic acid (1.10 mmol) in acetic acid (20 mL) was refluxed in the presence of ammonium acetate (0.28 mmol) under a N_2 atmosphere for about 24 h. Then, water was added and extracted with CH_2Cl. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with 1:10 (v/v) methanol/chloroform to yield as a dark red solid.

2. Tables and figures.

Table S1. Summary of photophysical data and energy levels.

Dye	λ_{max}[a] (ε) nm (10^4 $M^{-1}cm^{-1}$)		λ_{max}[b] nm		λ_{cutoff}[a] nm	E_{HOMO}/E_{LUMO} eV		E_g[c] eV	E_g[d] eV
						E_{exp}[c]	E_{cal}[d]		
on2	295 (3.19)	453 (1.03)	355	425	572	-5.70/-2.99	-5.65/-2.81	2.71	2.84
mn2	294 (4.56)	450 (1.11)	357	429	578	-5.72/-2.99	-5.67/-2.82	2.73	2.85
pn2	294 (2.33)	469 (0.72)	360	429	569	-5.69/-2.98	-5.59/-2.82	2.71	2.77
ob8	295 (4.23)	443 (1.49)	361	429	557	-5.74/-3.05	-5.72/-2.92	2.69	2.80
mb8	294 (4.82)	445 (1.53)	359	430	557	-5.76/-2.99	-5.74/-2.93	2.77	2.81
pb8	295 (3.43)	439 (1.11)	355	427	547	-5.78/-3.00	-5.65/-2.93	2.78	2.72

a Data is measured in DCM solvent. b Data are measured on TiO_2 films. c Data are measured from CV diagram. d Data are calculated by B3LYP/6-311G(d,p).

Table S2. The six dyes of electron transitions in CAM-B3LYP/6-31G(d) level.

dye	transition	λ_{abs}		f	main composition
		nm	eV		
on2	s_0-s_1	395.40	3.14	0.77	H→L (83.1%); H-1→L (7.1%)
	s_0-s_2	303.24	4.09	0.34	H-3→L (55.3%); H-4→L (17.4%)
	s_0-s_3	285.21	4.35	0.24	H→L+1 (41.0%); H-4→L (15.3%)
mn2	s_0-s_1	393.88	3.15	0.76	H→L (83.1%); H-1→L (6.3%)
	s_0-s_2	302.64	4.10	0.35	H-3→L (51.2%); H-4→L (21.8%)
	s_0-s_3	284.13	4.36	0.24	H→L+1 (37.5%); H→L+4 (17.6%)
pn2	s_0-s_1	395.46	3.14	0.80	H→L (57.1%); H-1→L (32.8%)
	s_0-s_2	303.52	4.08	0.41	H-3→L (52.3%); H-4→L (16.2%)
	s_0-s_3	288.04	4.30	0.25	H→L+1 (45.6%); H-4→L (18.9%)
ob8	s_0-s_1	387.66	3.20	0.46	H→L (49.3%); H-1→L (40.5%)
	s_0-s_2	308.15	4.02	0.42	H-3→L (51.3%); H-4→L 24.2%)
	s_0-s_3	282.86	4.38	0.31	H-4→L (21.1%); H→L+1 (14.4%)
mb8	s_0-s_1	383.18	3.24	0.43	H-1→L (80.9%); H→L (7.8%)
	s_0-s_2	307.61	4.03	0.43	H-3→L (45.1%); H-4→L (31.6%)
	s_0-s_3	282.24	4.39	0.12	H→L+2 (77.5%)
pb8	s_0-s_1	384.77	3.22	0.45	H-1→L (61.9%); H→L (27.8%)
	s_0-s_2	308.10	4.02	0.47	H-3→L (47.9%); H-4→L (25.8%)
	s_0-s_3	286.22	4.33	0.33	H→L (33.9%); H-4→L (29.9%)

Table S3. The fitting τ and corresponding A of the six new dyes from TRPL.

Dye	DCM/TiO_2					η_{inj} [b] (ns)
	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{av} [a] (ns)	
on2	81.40/92.80	2.02/0.10	18.60/7.20	7.23/7.91	2.99/0.66	77.93
mn2	63.05/91.05	2.03/0.11	36.95/8.95	7.46/5.54	4.04/0.60	85.15
pn2	64.28/84.78	1.73/0.12	35.72/15.22	5.44/3.37	3.06/0.61	80.07
ob8	93.29/89.19	2.36/0.21	6.71/10.81	9.48/2.57	2.84/0.47	83.45
mb8	89.20/90.68	2.43/0.27	10.80/9.32	7.99/2.66	3.03/0.49	83.83
pb8	91.17/91.77	2.52/0.22	8.83/8.23	8.81/3.47	3.08/0.49	84.09

[a] The values of τ_{av} are determined with $\tau_{av} = A_1\tau_1 + A_2\tau_2$. [b] Calculated by $\eta_{inj} = 1 - \tau_{TiO_2}/\tau_{DCM}$.

Table S4. Dihedral angle of six dyes and TiO_2@dyes in B3LYP/6-31G(d) level.

	dihedral angle	on2	mn2	pn2	ob8	mb8	pb8
dye	**Cz-PTZ**	79.18	82.90	81.84	77.73	83.92	82.94
	PTZ-CA	17.48	17.59	17.60	16.34	16.76	16.71
	Cz-CA	84.56	66.26	75.56	86.03	68.37	77.59
	μ	7.87	8.48	7.59	6.65	6.82	6.14
	μx	7.86	5.03	4.75	6.64	3.62	3.09
dye_{TiO2}	**Cz-PTZ**	78.01	83.40	81.18	72.53	88.14	83.97
	PTZ-CA	25.69	25.33	26.27	23.57	23.06	24.36
	Cz-CA	75.99	66.08	84.72	84.47	78.30	89.75
	μ	12.44	12.40	12.70	14.58	14.45	14.08
	μx	12.38	8.92	9.84	14.14	8.56	10.12

Table S5. The adsorption energies *E*ads of the optimized dye/$(TiO_2)_{16}$ systems.

Dye	E_{total} (a.u.)	E_{TiO2} (a.u.)	E_{dye} (a.u.)	ΔE_{ads} (eV)
on2	-5439.663	-3340.260	-2099.118	-7.746
mn2	-5439.666	-3340.260	-2099.121	-7.755
pn2	-5439.666	-3340.260	-2099.122	-7.727
ob8	-5675.531	-3340.258	-2334.993	-7.619
mb8	-5675.534	-3340.259	-2334.993	-7.673
pb8	-5675.535	-3340.259	-2334.993	-7.700

Table S6. The EIS fitting parameters for DSSCs sensitized by the dyes.

Dye	R_s (Ω)	R_{pt} (Ω)	R_{rec} (Ω)
on2	12.69	2.93	26.76
mn2	17.02	3.76	30.09
pn2	10.67	3.10	23.58
ob8	10.13	2.81	28.33
mb8	12.08	3.98	31.82
pb8	10.61	7.96	24.92

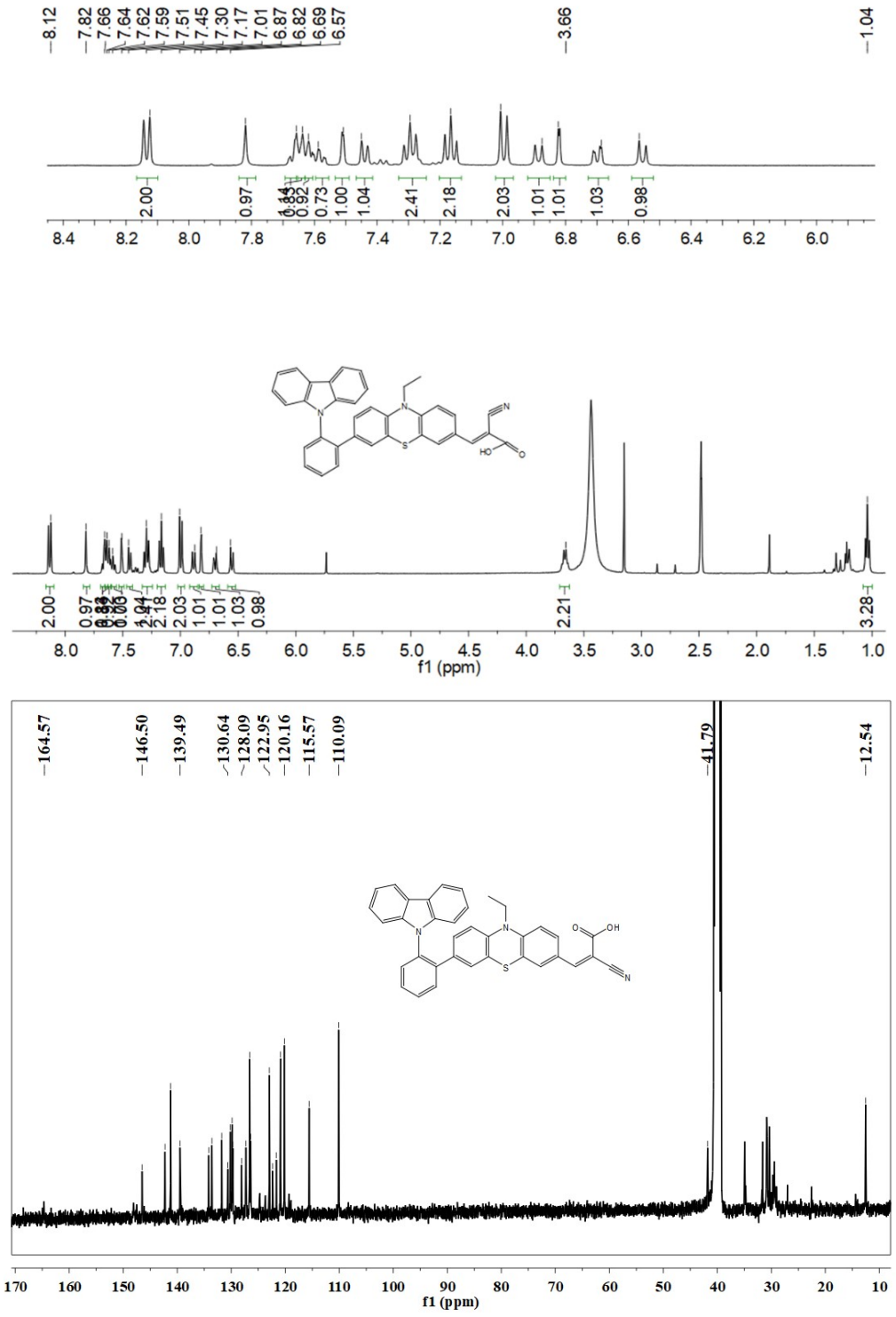


Figure S1. (a) ^{1}H NMR and (b) ^{13}C NMR of **on2** dye.

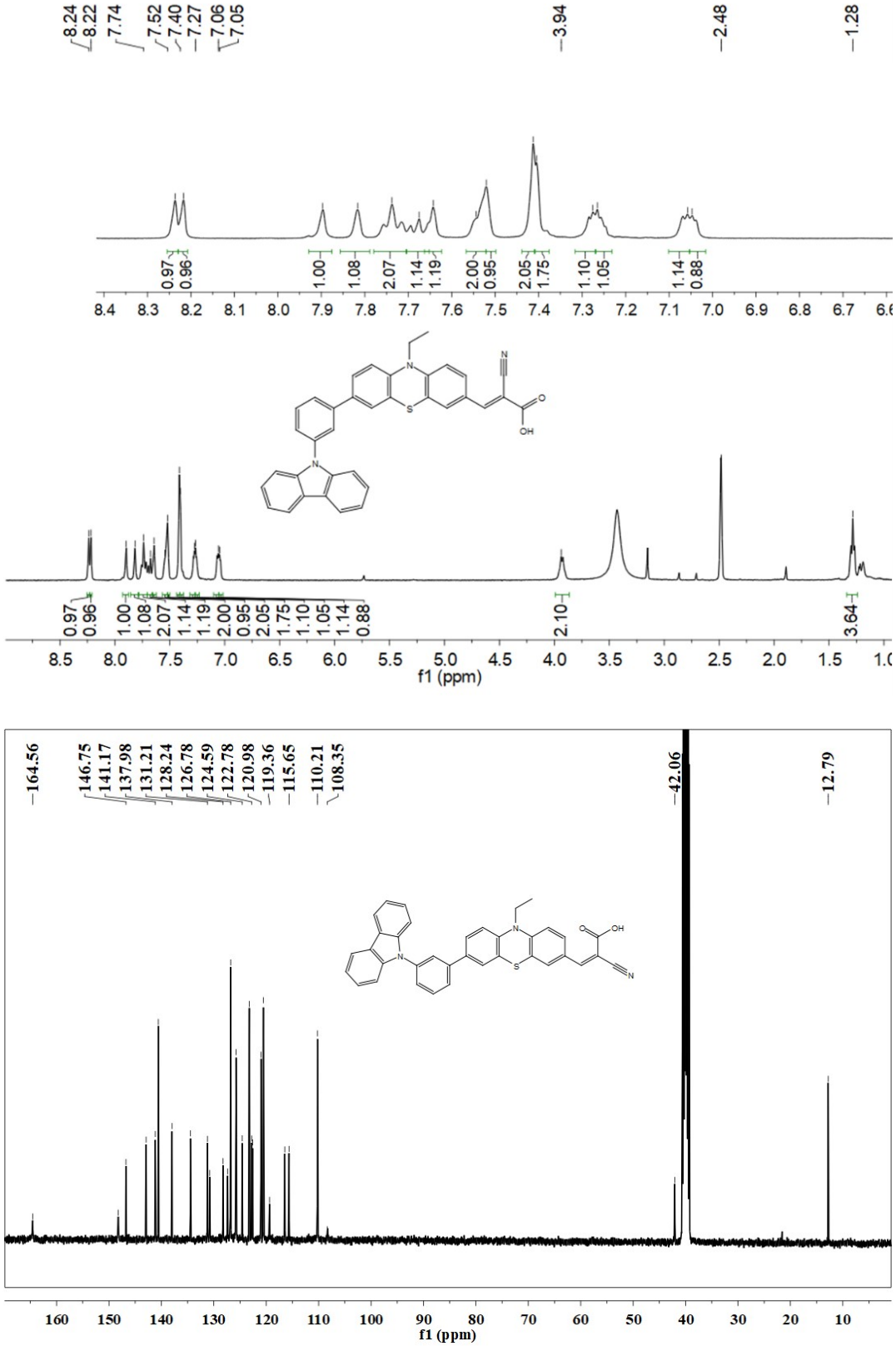


Figure S2. (a) ^{1}H NMR and (b) ^{13}C NMR of **mn2** dye.

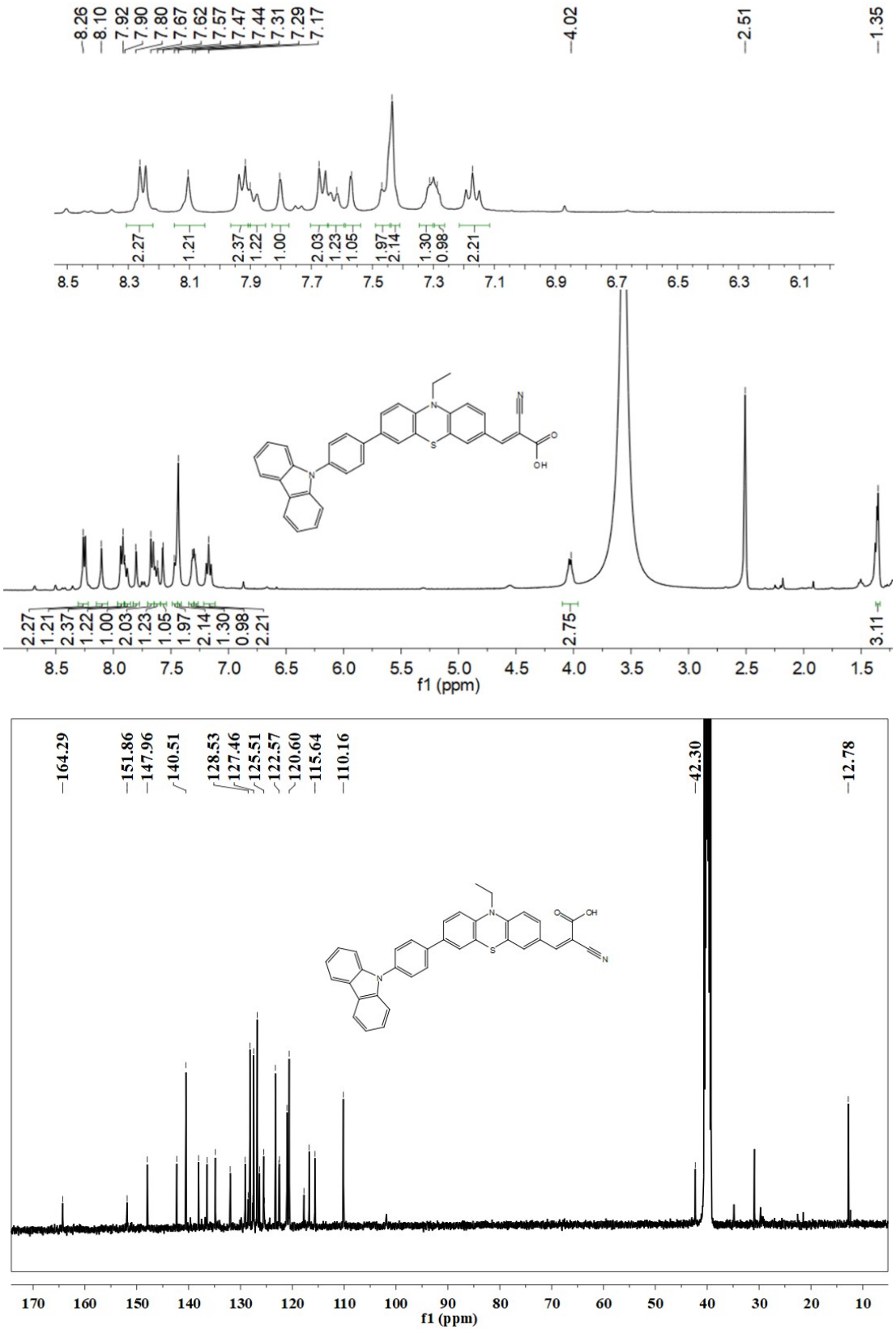
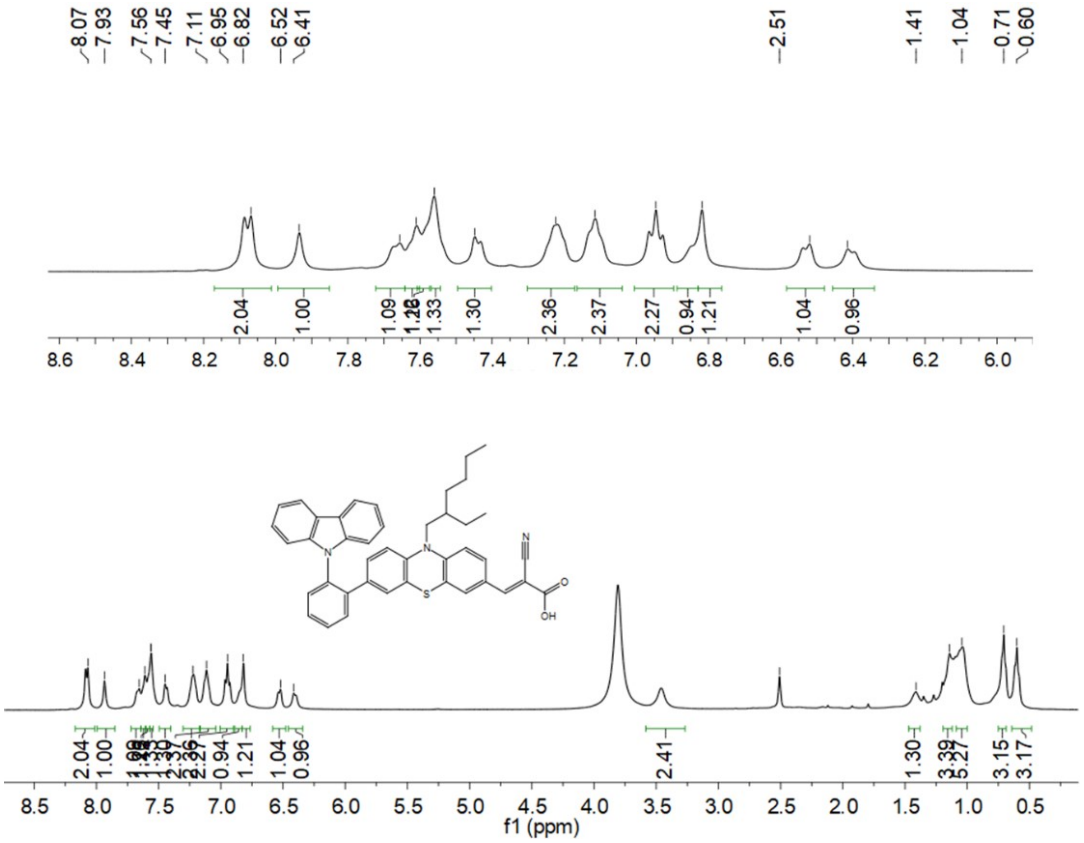


Figure S3. (a) ^{1}H NMR and (b) ^{13}C NMR of **pn2** dye.



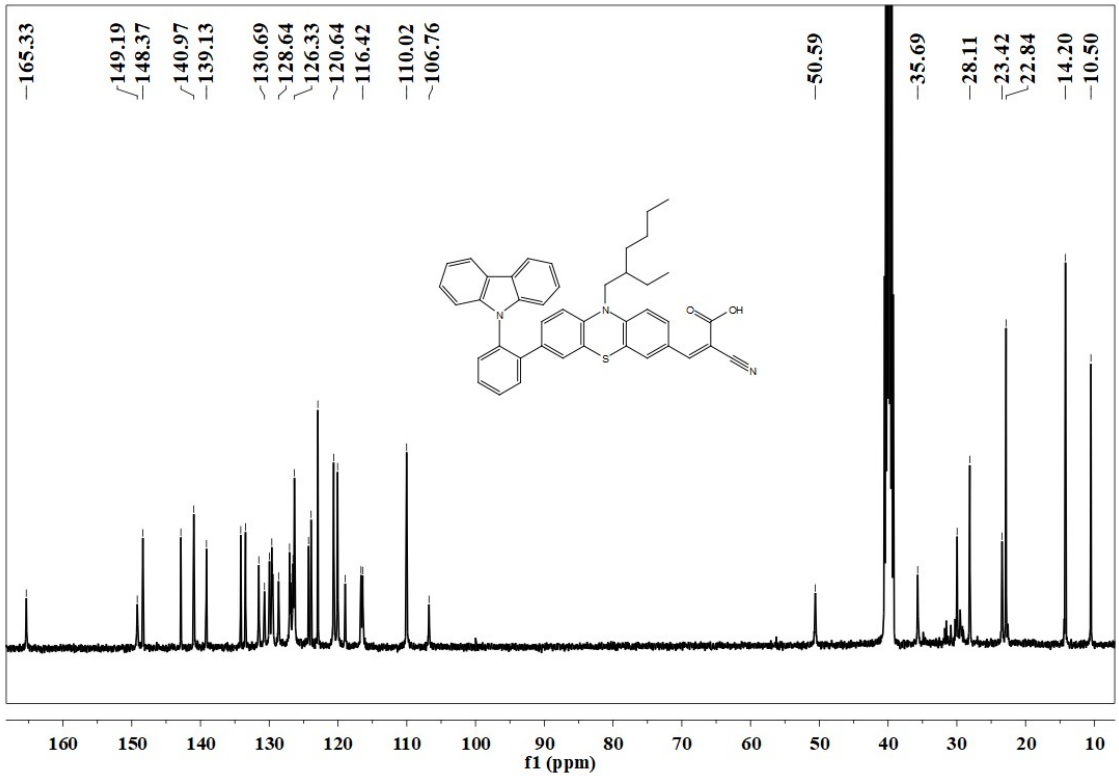


Figure S4. (a) ^{1}H NMR and (b) ^{13}C NMR of **ob8** dye.

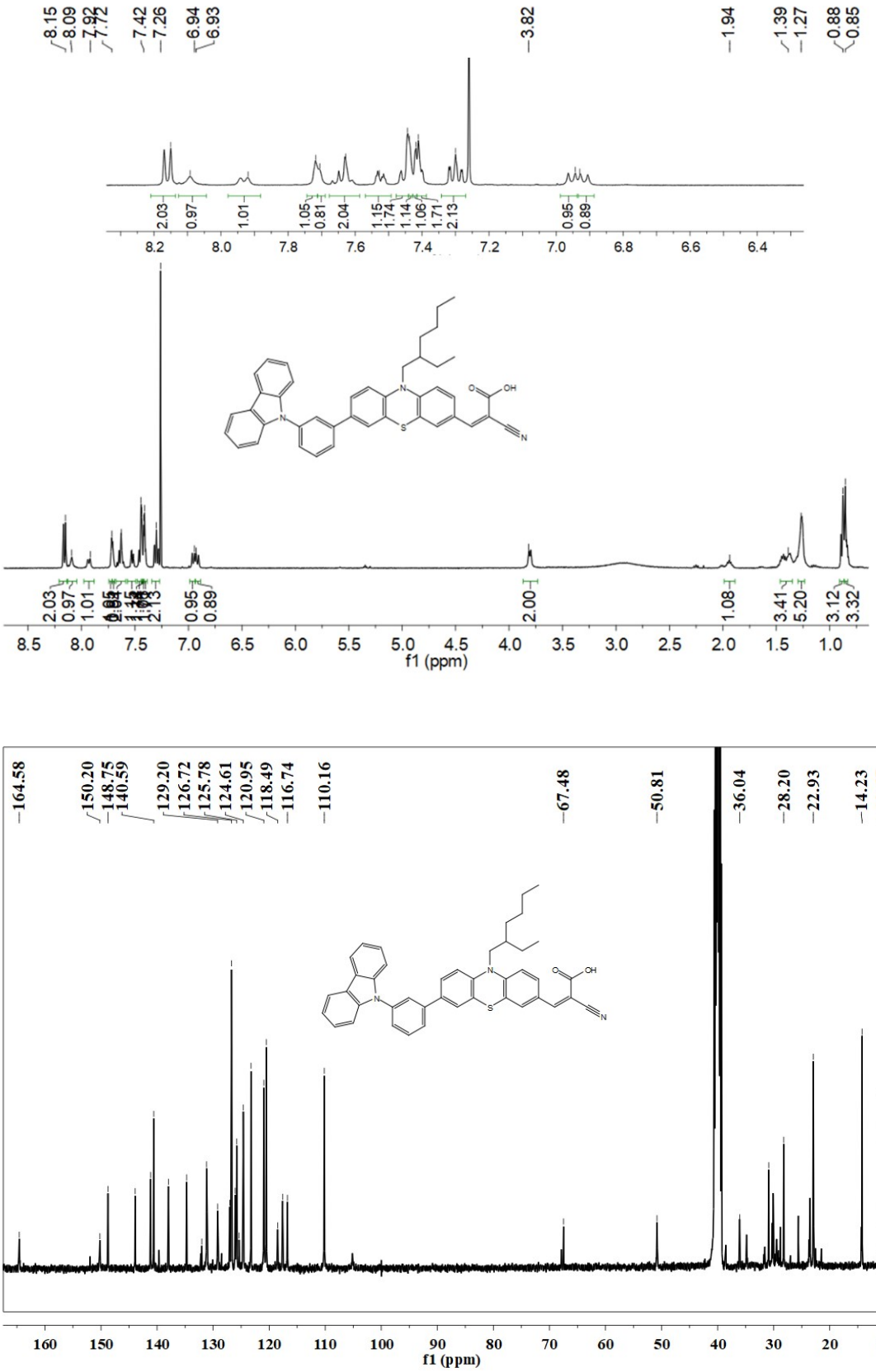


Figure S5. (a) ^{1}H NMR and (b) ^{13}C NMR of **mb8** dye.

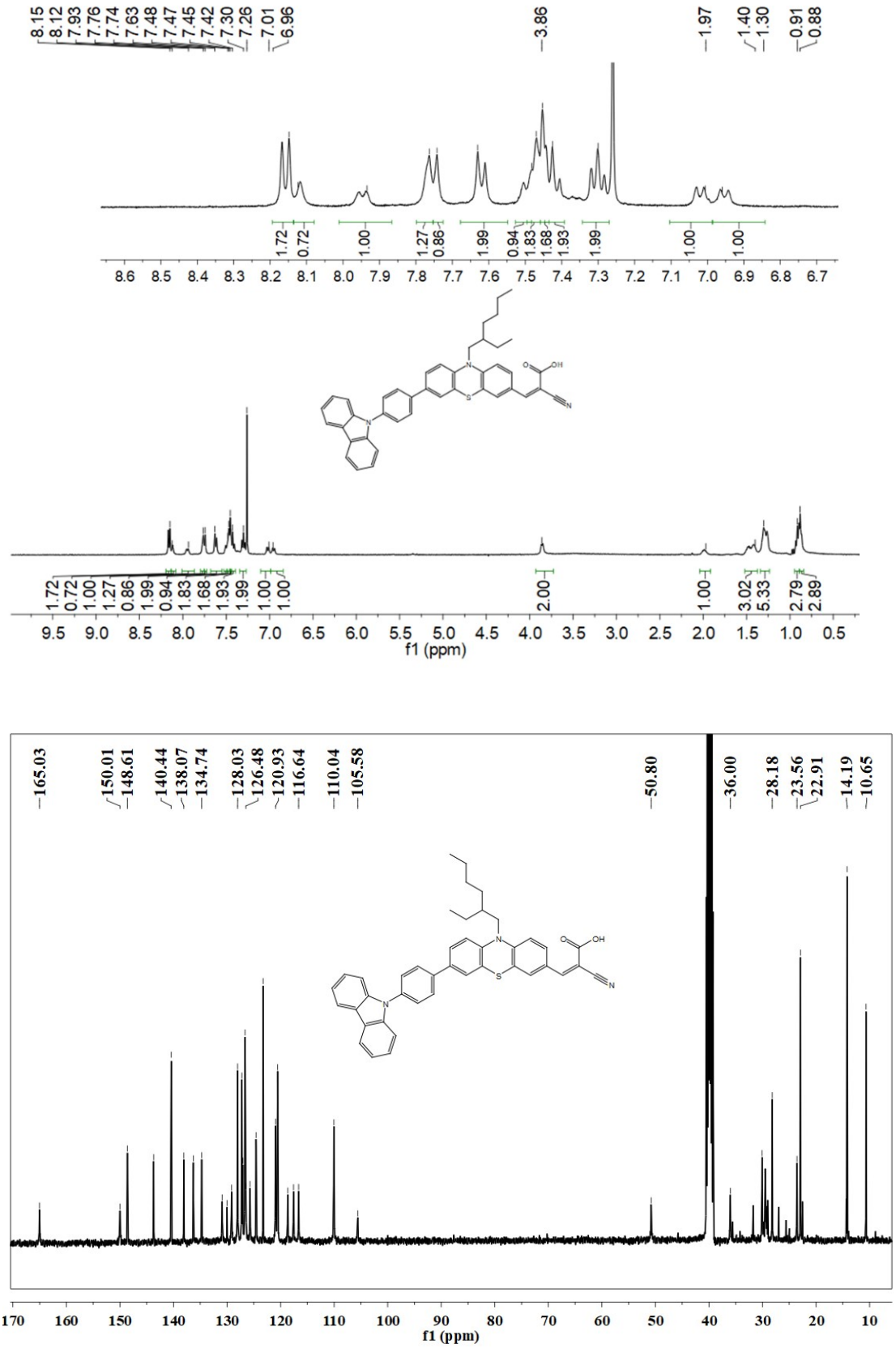


Figure S6. (a) ^{1}H NMR and (b) ^{13}C NMR of **pb8** dye.

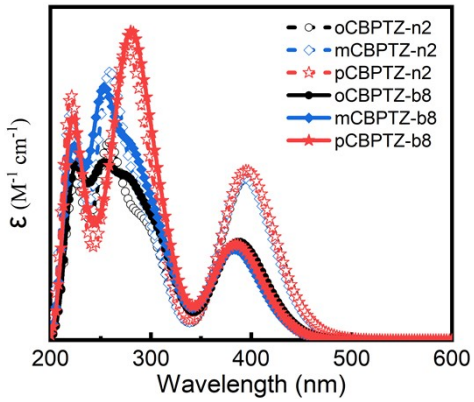


Figure S7. Calculated UV-Vis absorbance spectra of six dyes in THF.

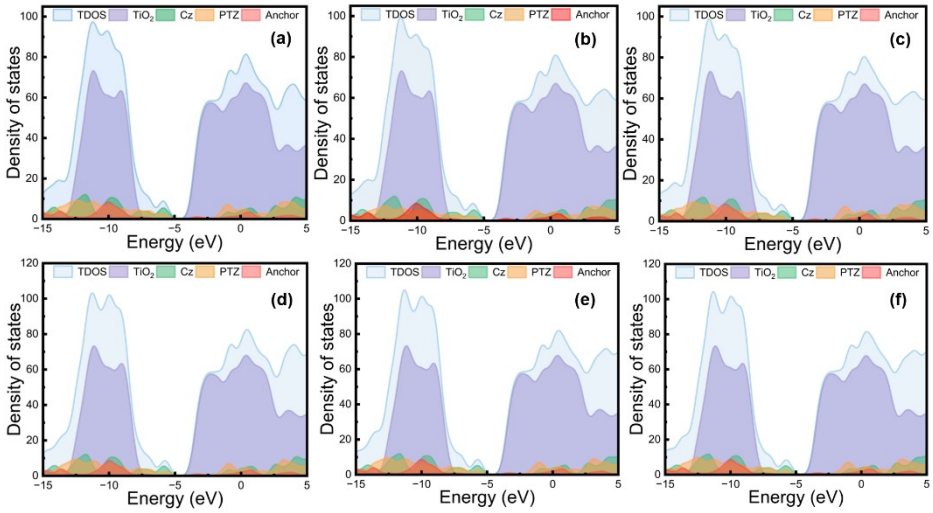


Figure S8. Calculated projected density of states (PDOS) for (a) **on2**, (b) **mn2**, (c) **pn2**, (d) **ob8**, (e) **mb8**, (f) **pb8**.

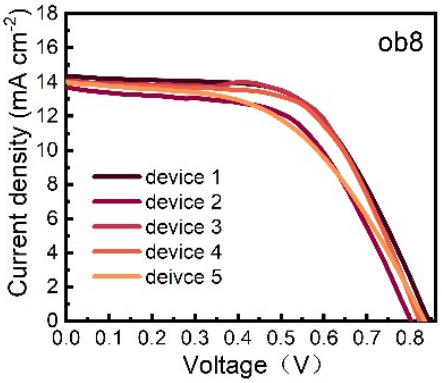


Figure S9. The *J-V* curves of **ob8** device for reproducibility test.

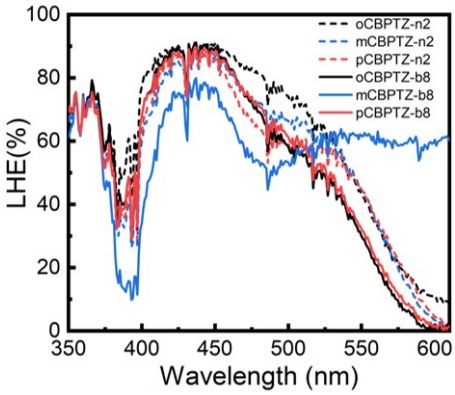


Figure S10. LHE spectra of the dye-grafted TiO_2 films of six dyes. The equation: $LHE_{(\lambda)} = 1 - 10^{-A\lambda}$, where A is the absorbance of the dye, λ is the global spectral irradiance (W/sm/nm).

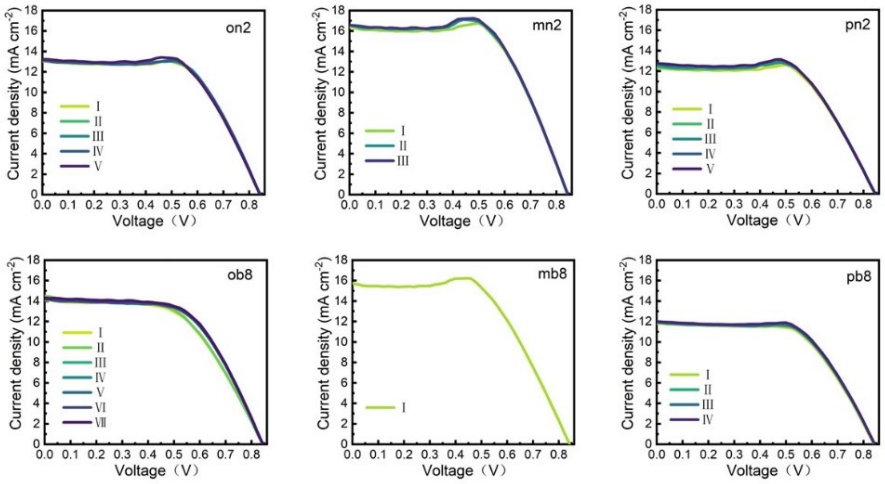


Figure S11. *J-V* curves for repeated testing of the same device within 24 h, the Roman numerals are the times for testing.

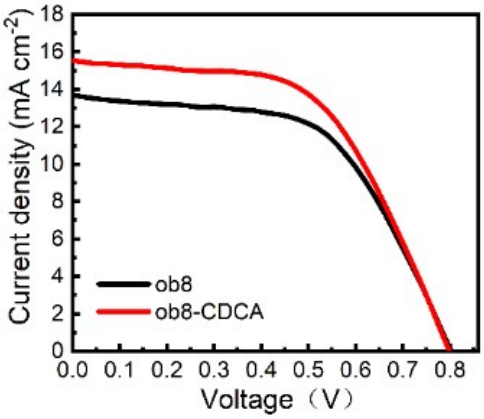


Figure S12. The *J-V* curves of **ob8** and **ob8-CDCA** co-adsorbent device.