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Electronic Supplementary Information

Organic Dyes Containing Oligo-Phenothiazine for Dye-Sensitized Solar Cells†

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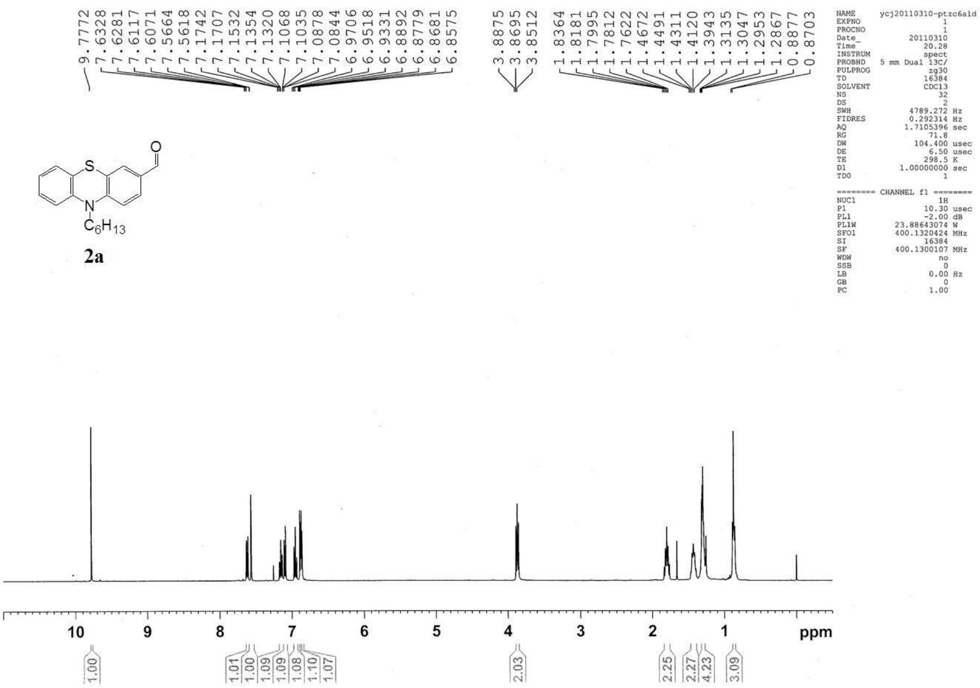


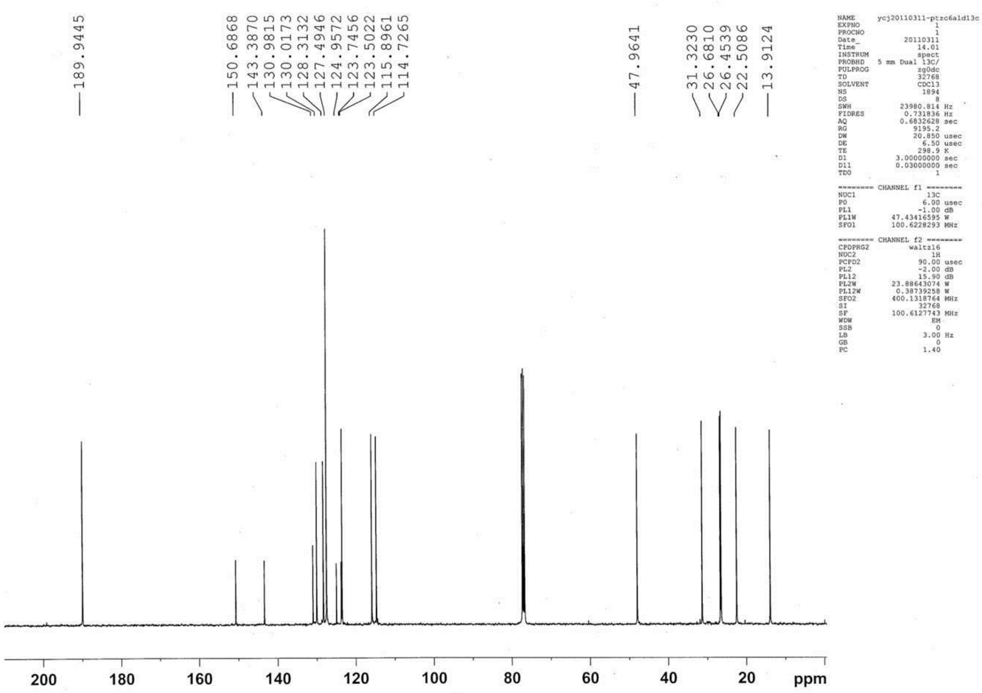
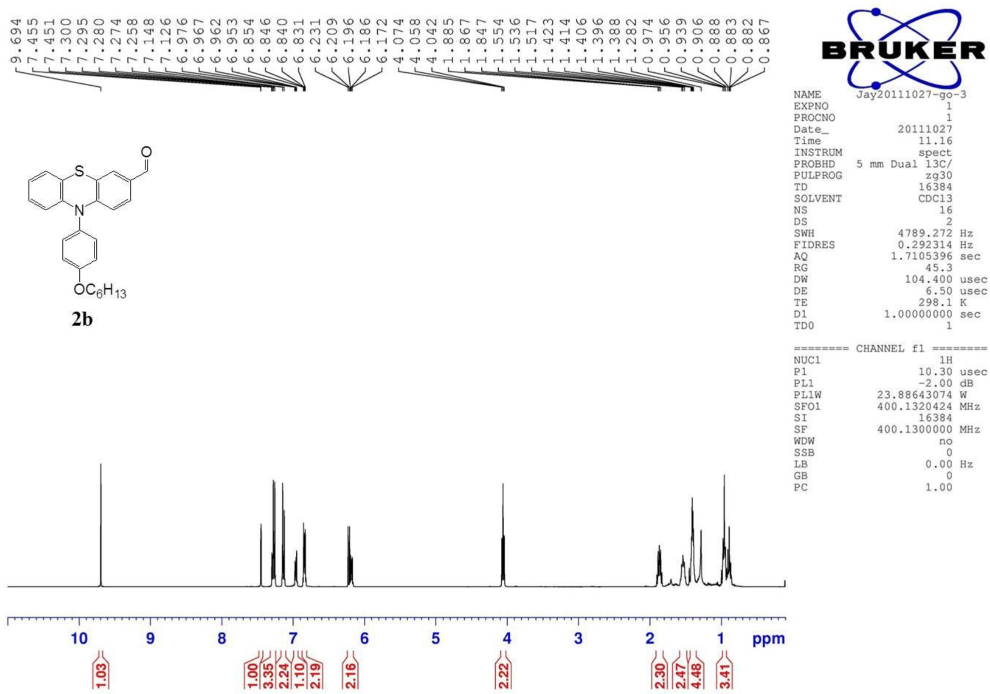


Fig. S1 [1]H NMR (upper) and [13]C NMR (lower) spectra of **2a** in $CDCl_3$.



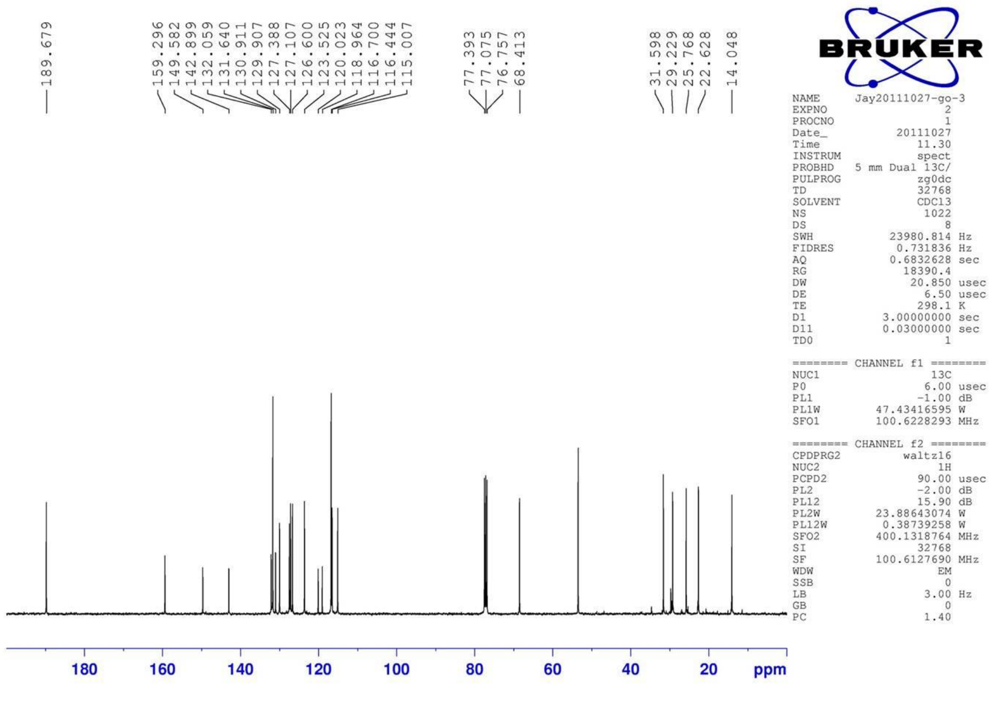


Fig. S2 ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **2b** in $CDCl_3$.

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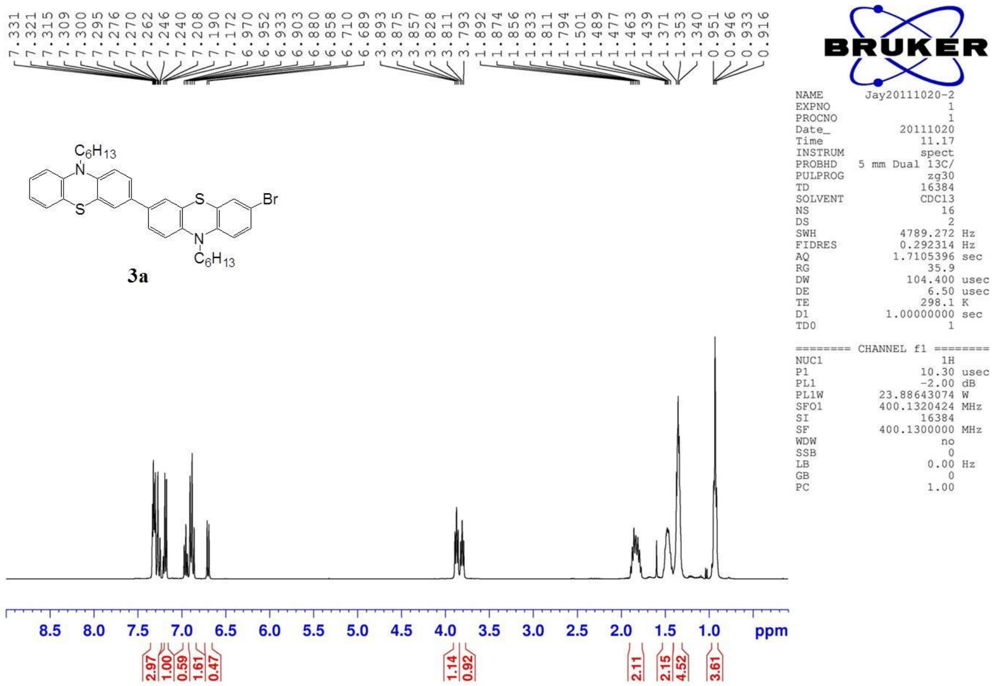

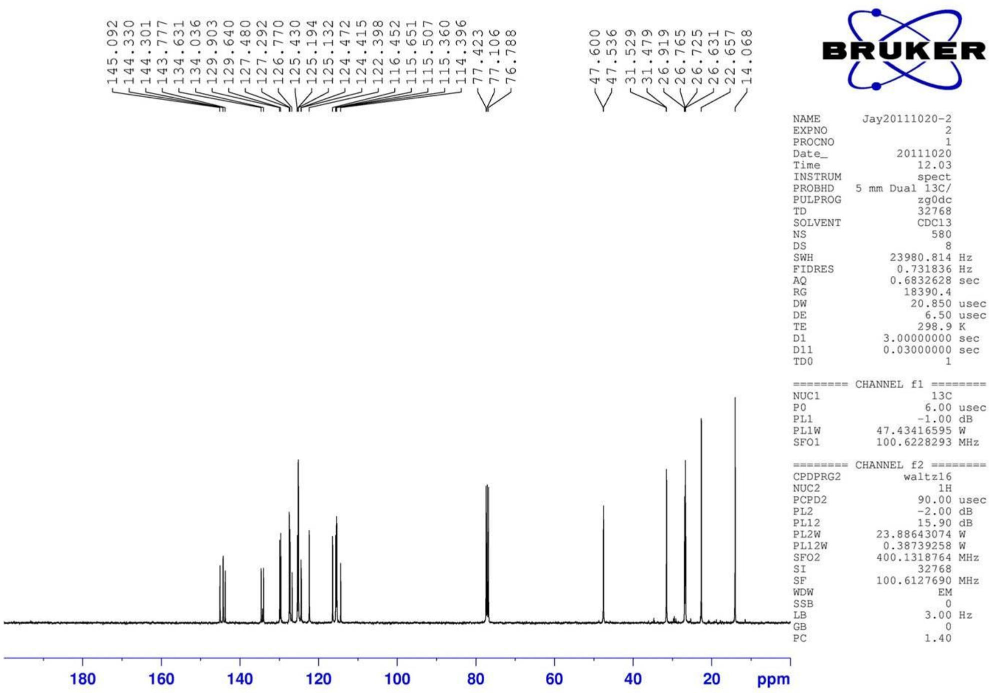

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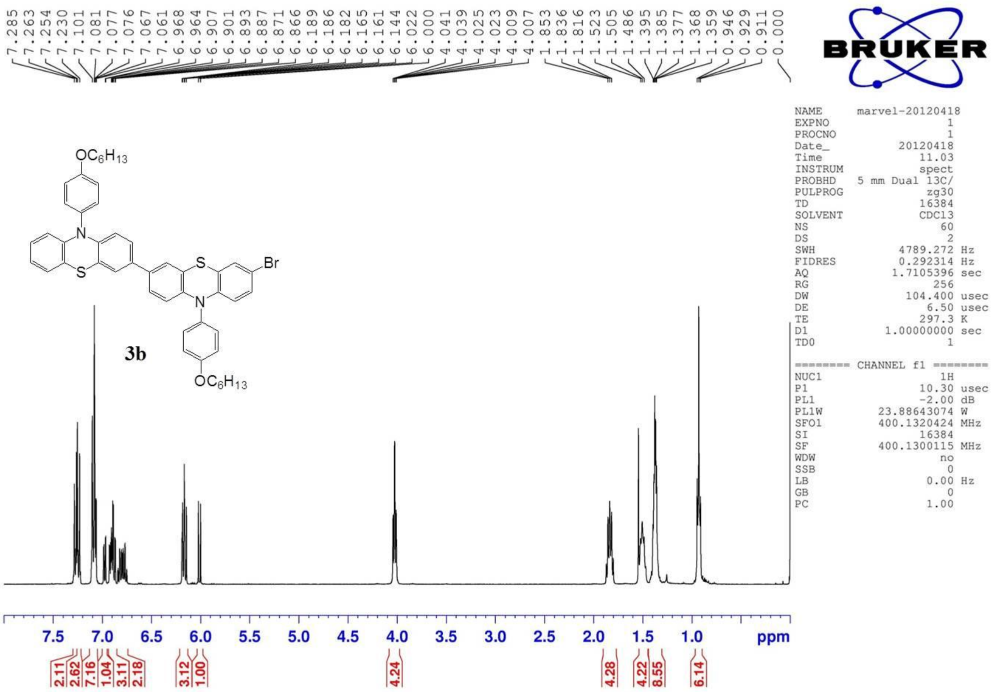


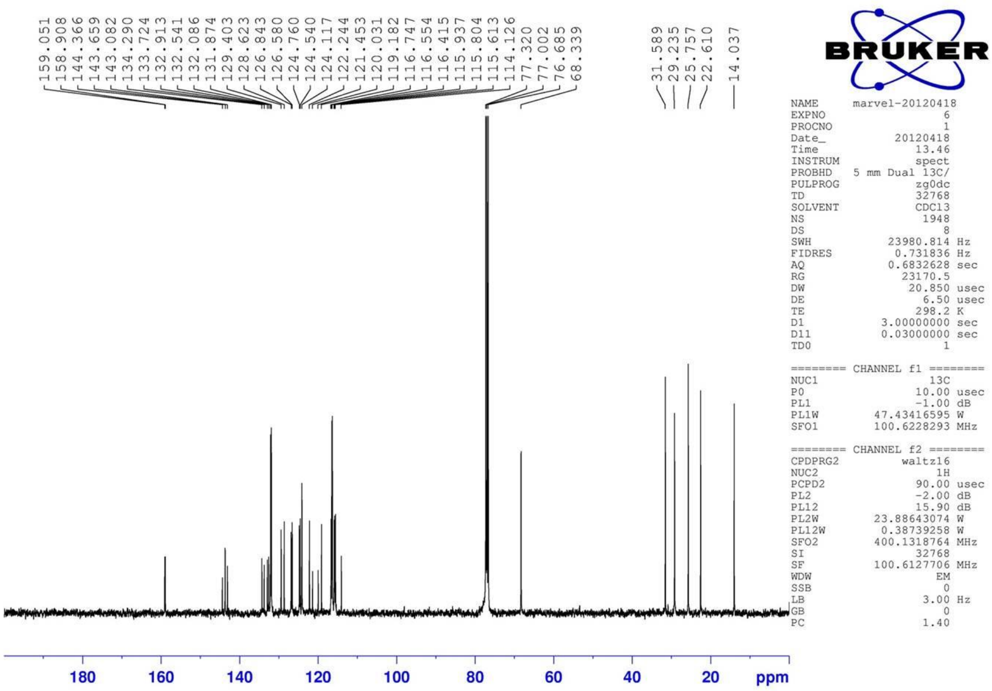
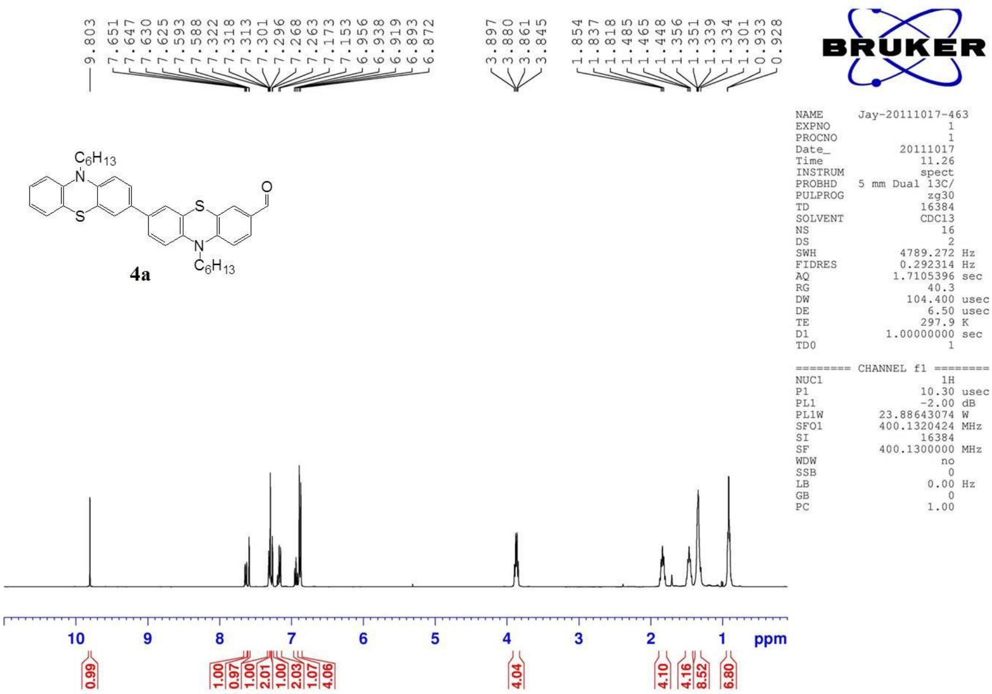
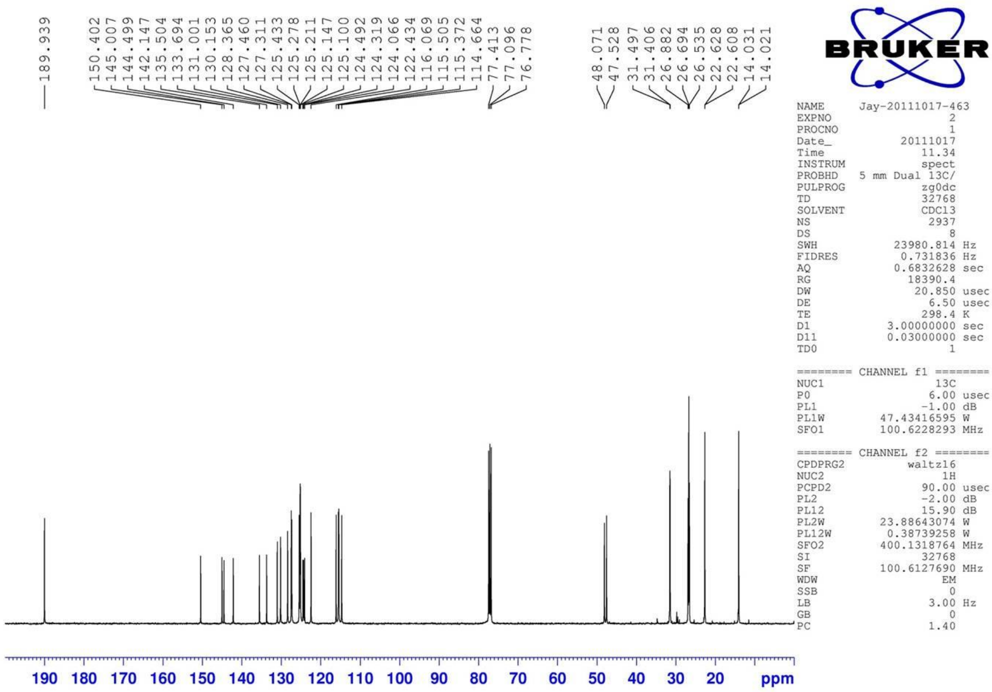


Fig. S4 ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **3b** in $CDCl_3$.





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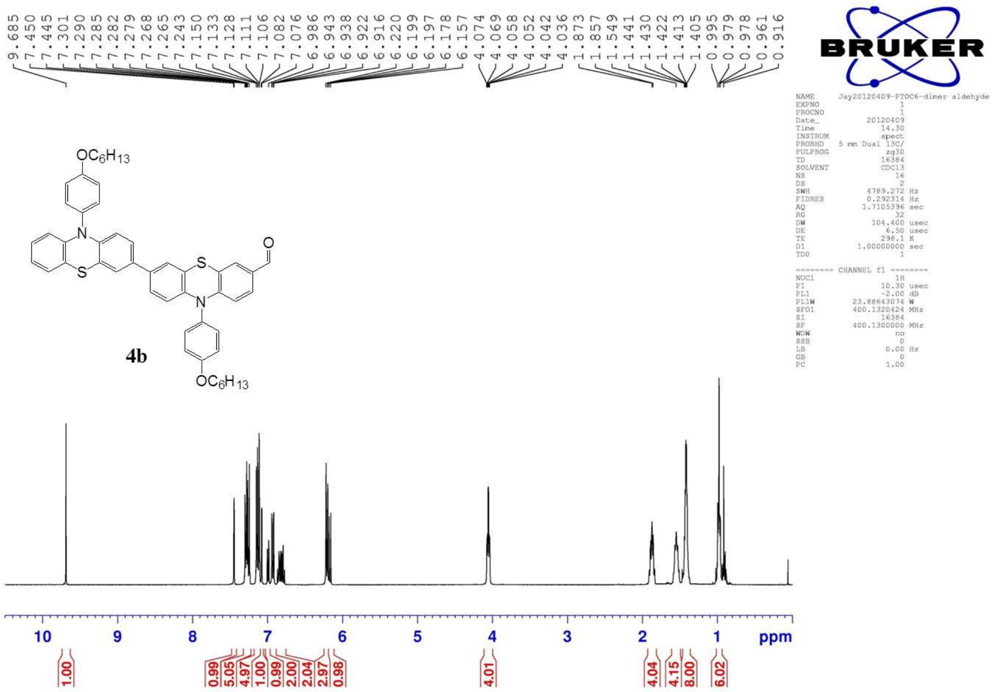

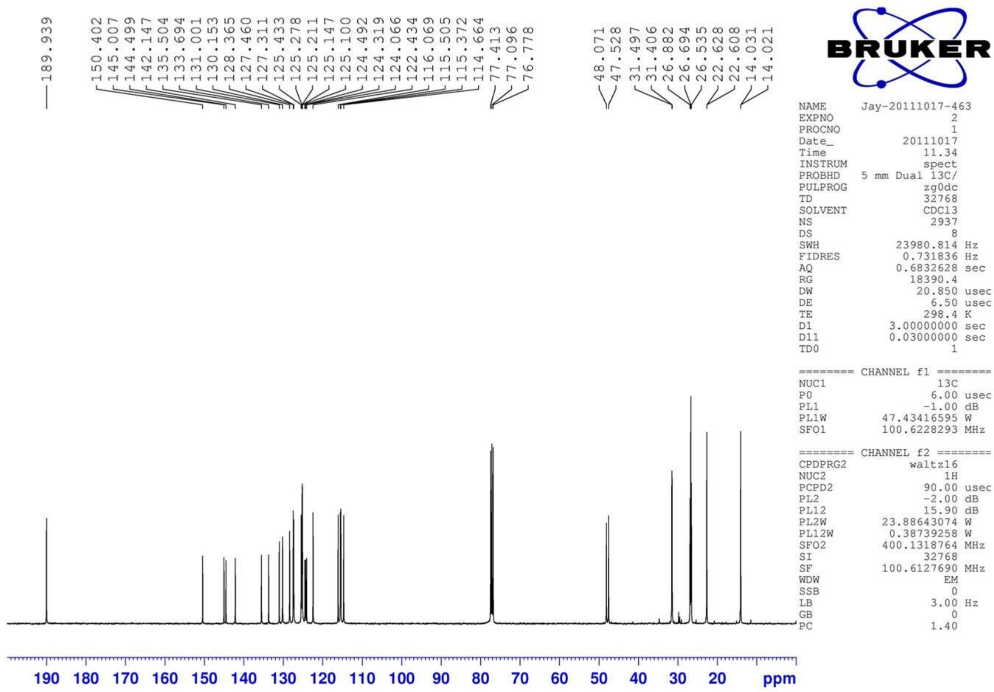

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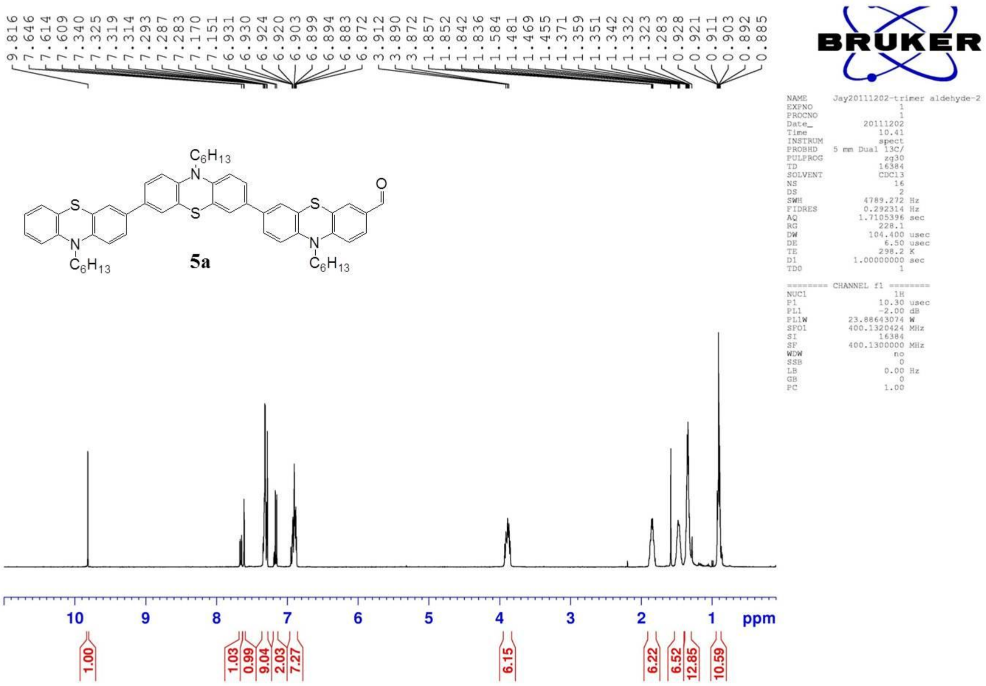

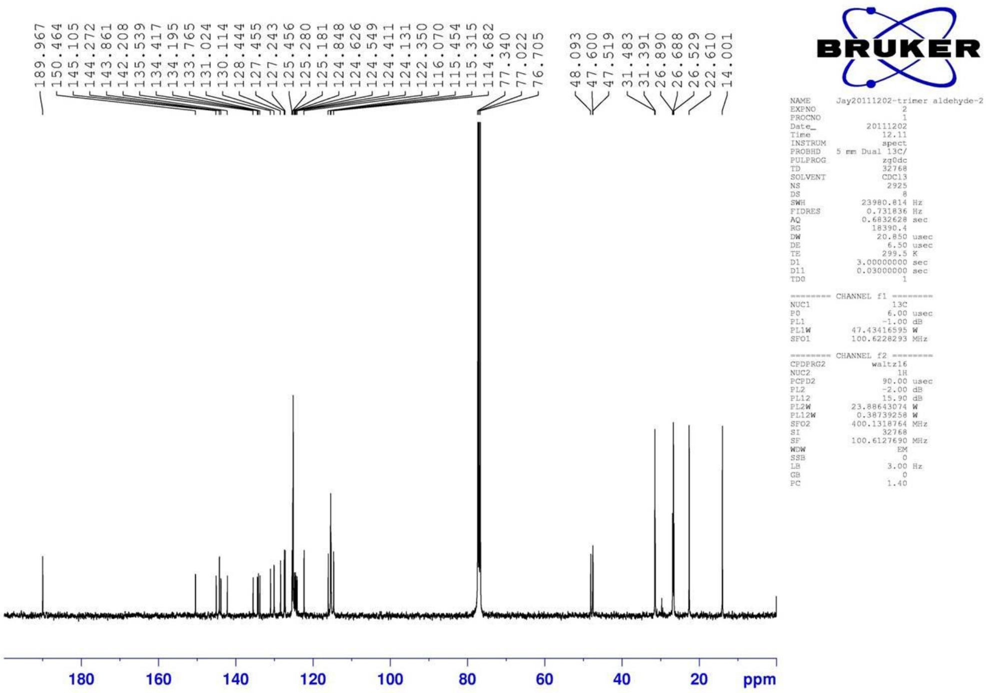

Fig. S7 ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **5a** in $CDCl_3$.

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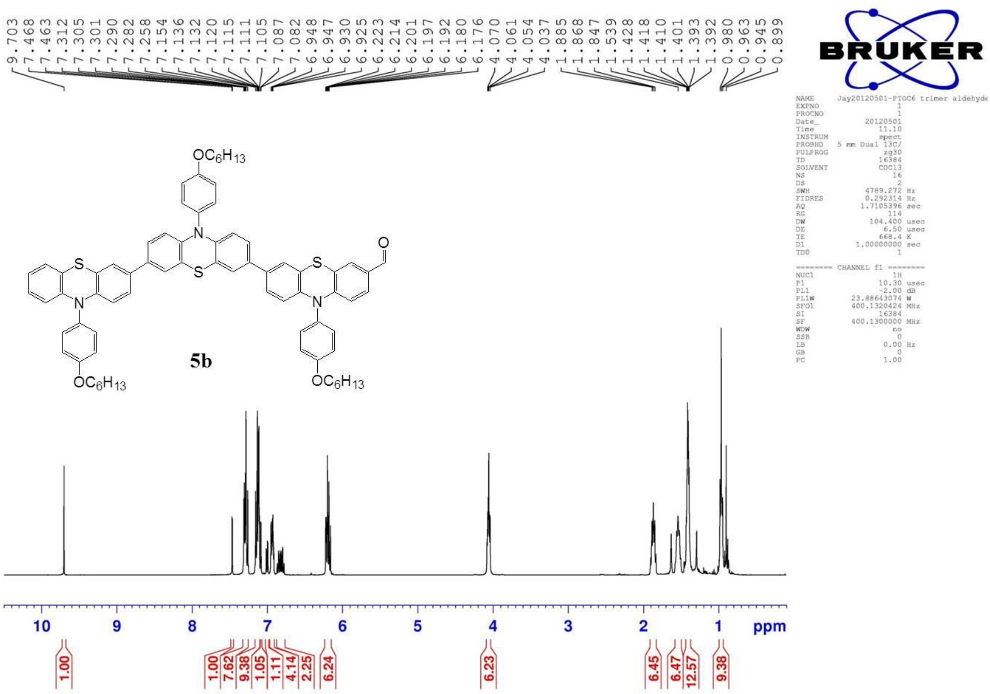

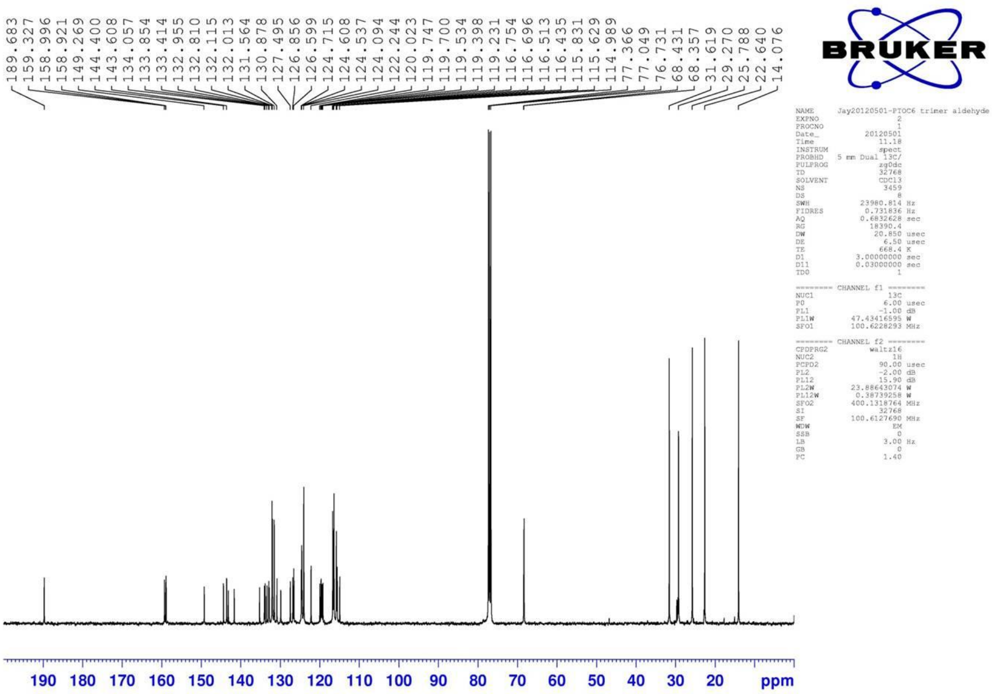

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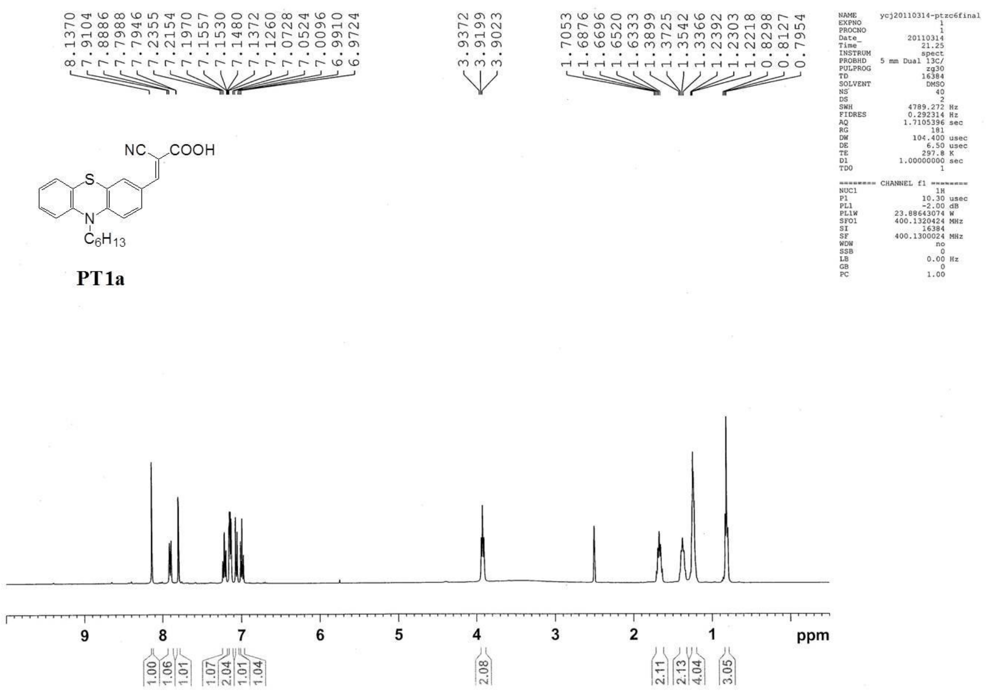


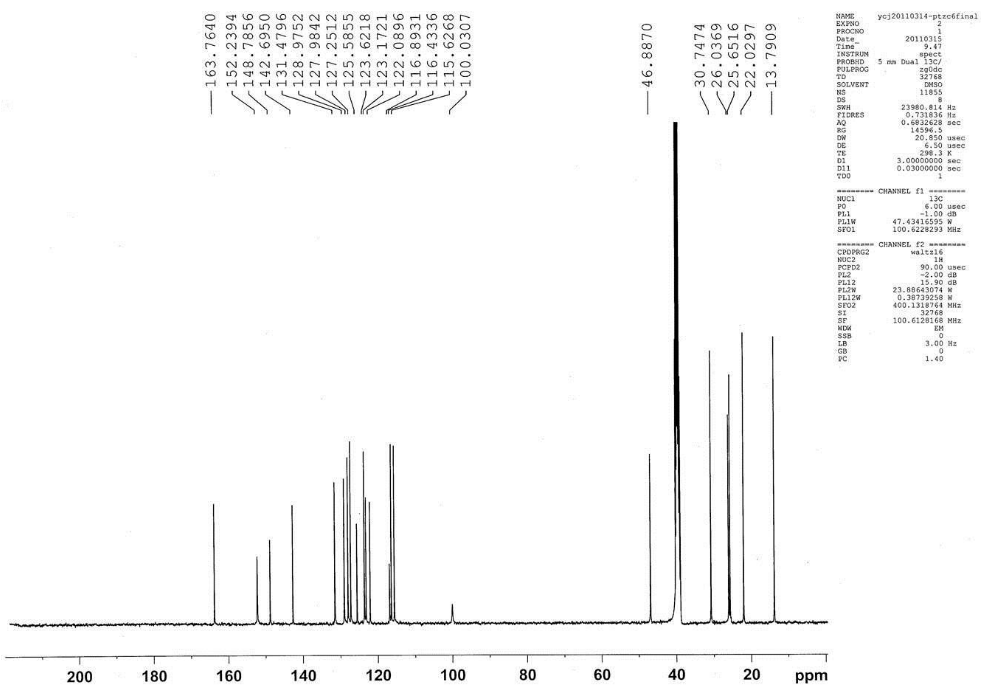
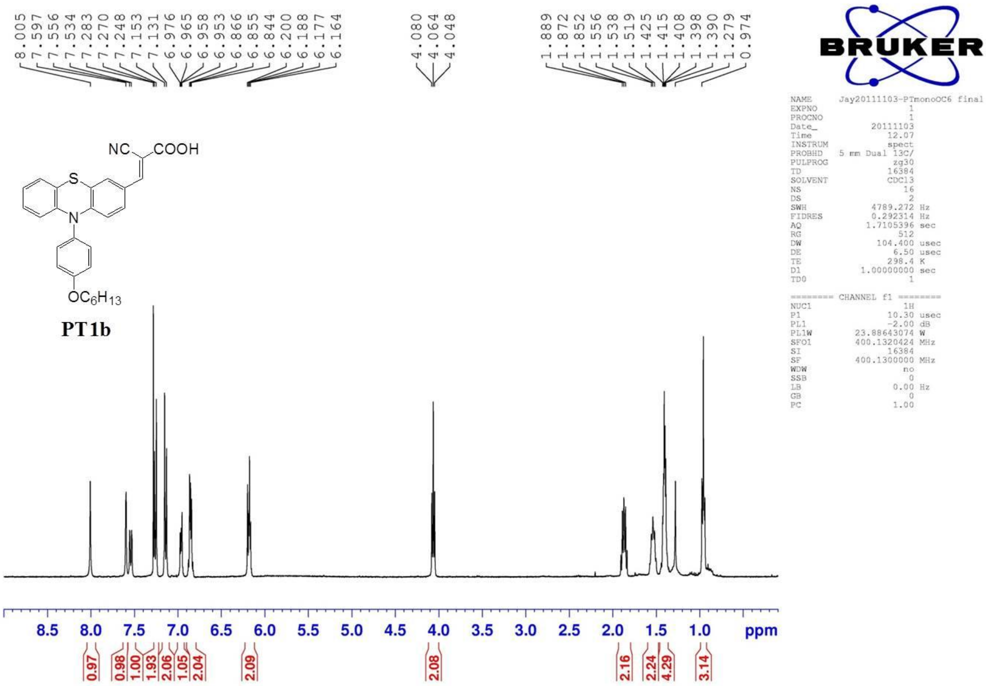
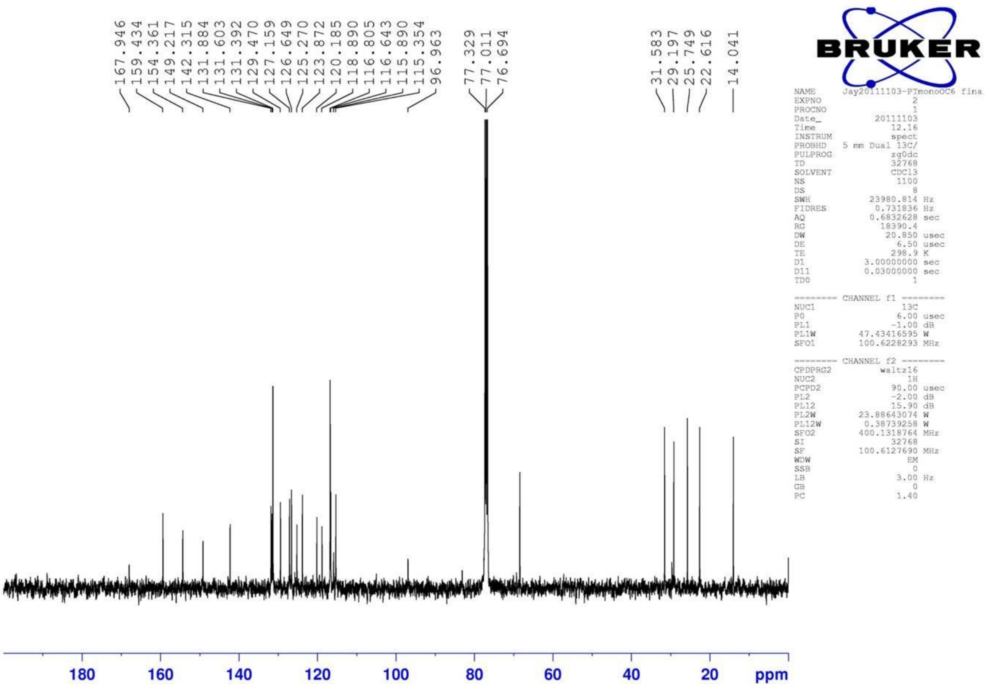


Fig. S9 ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PT1a** in DMSO-d_6.





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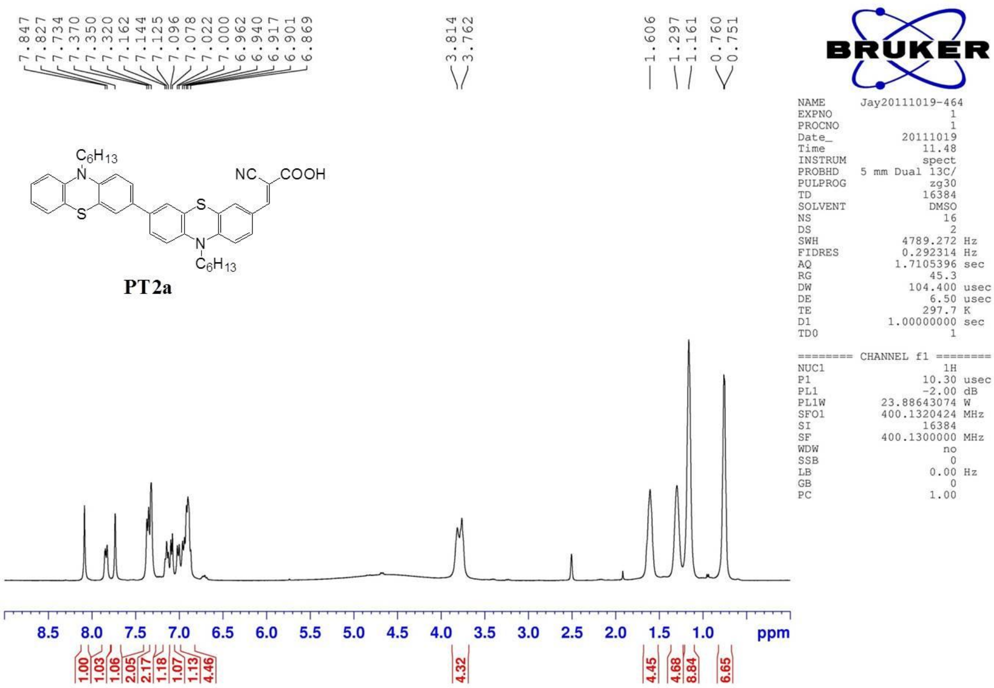

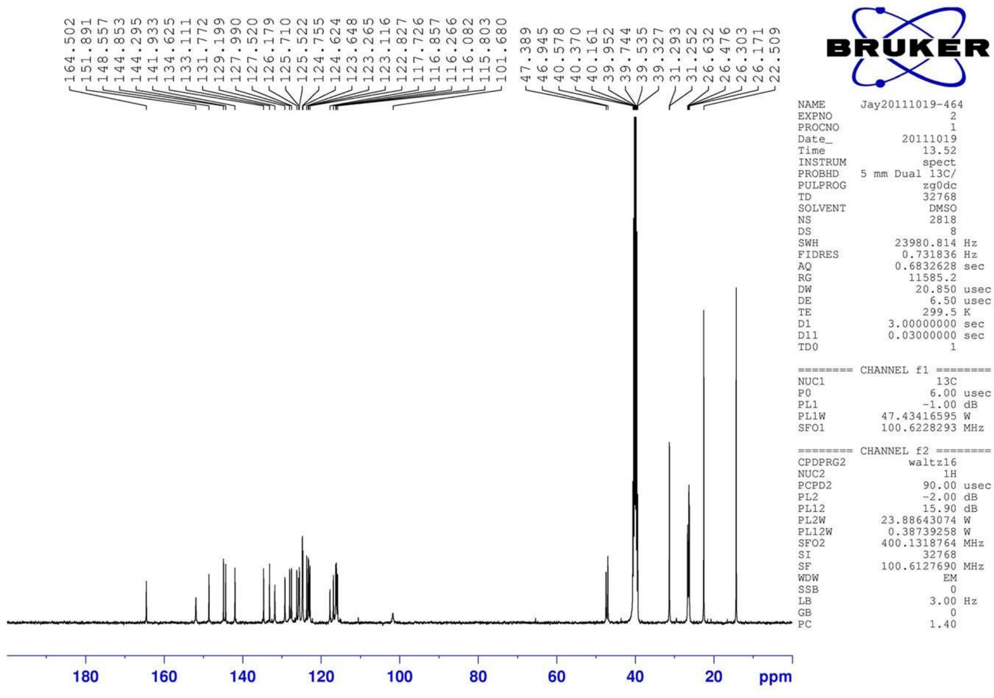

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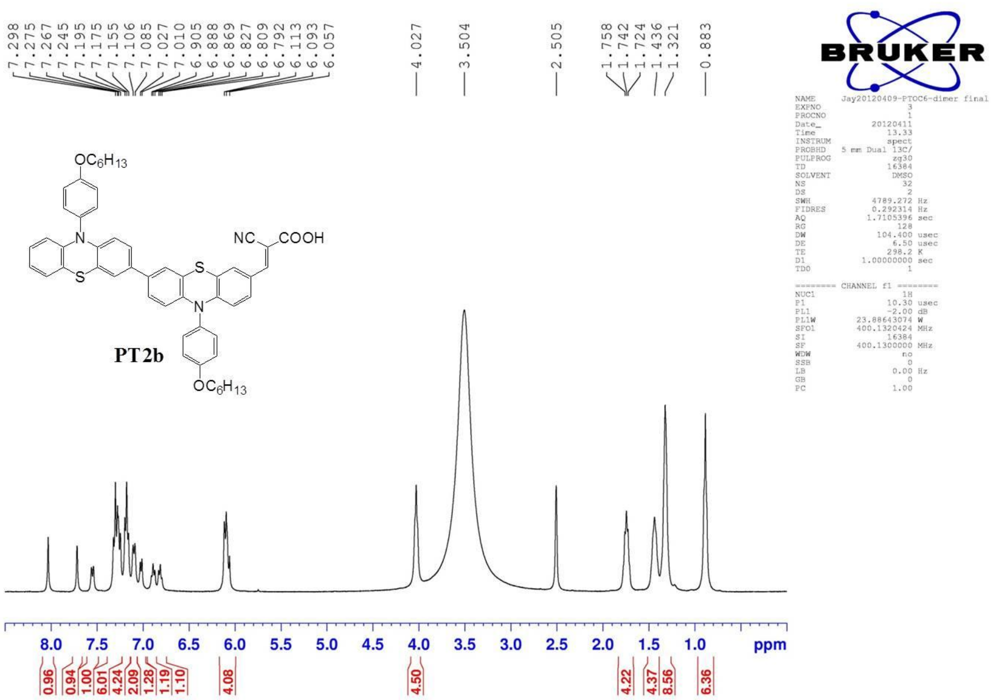


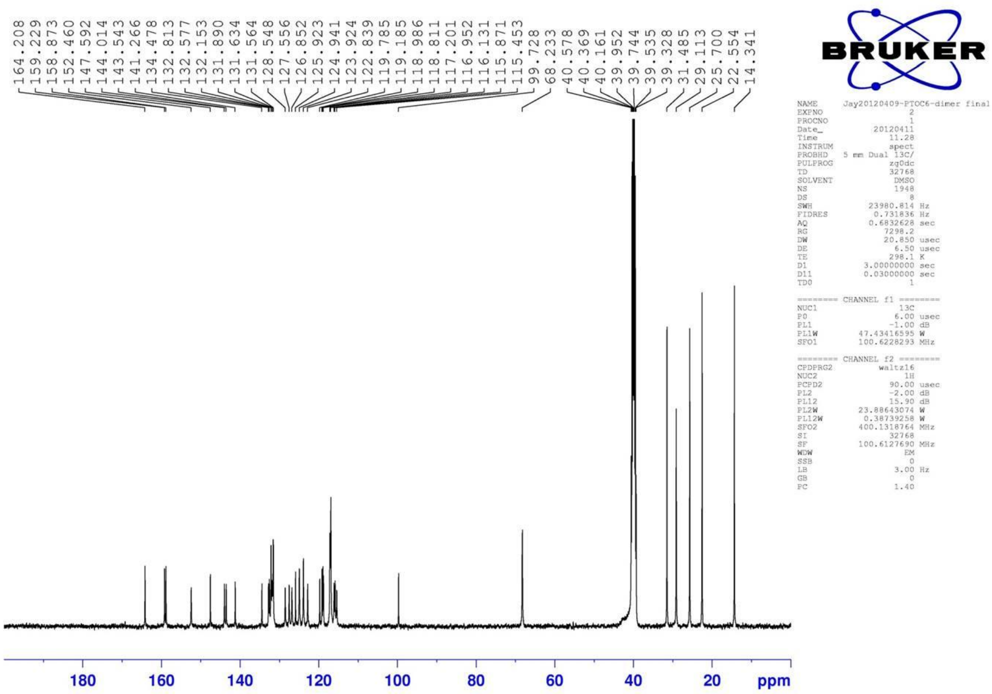
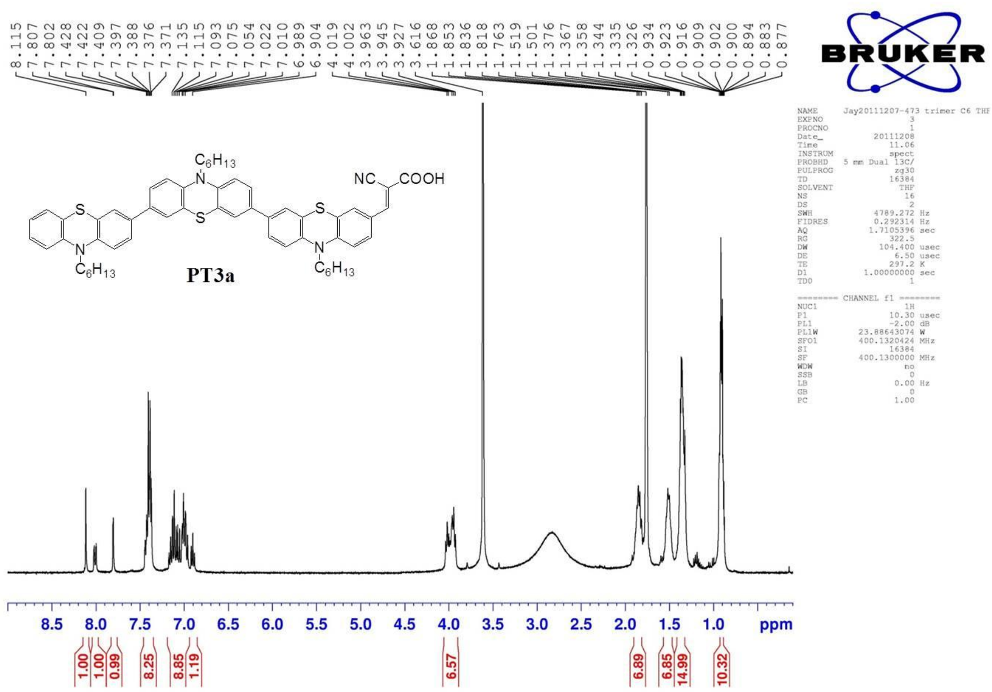


Fig. S12 ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PT2b** in DMSO-d_6.



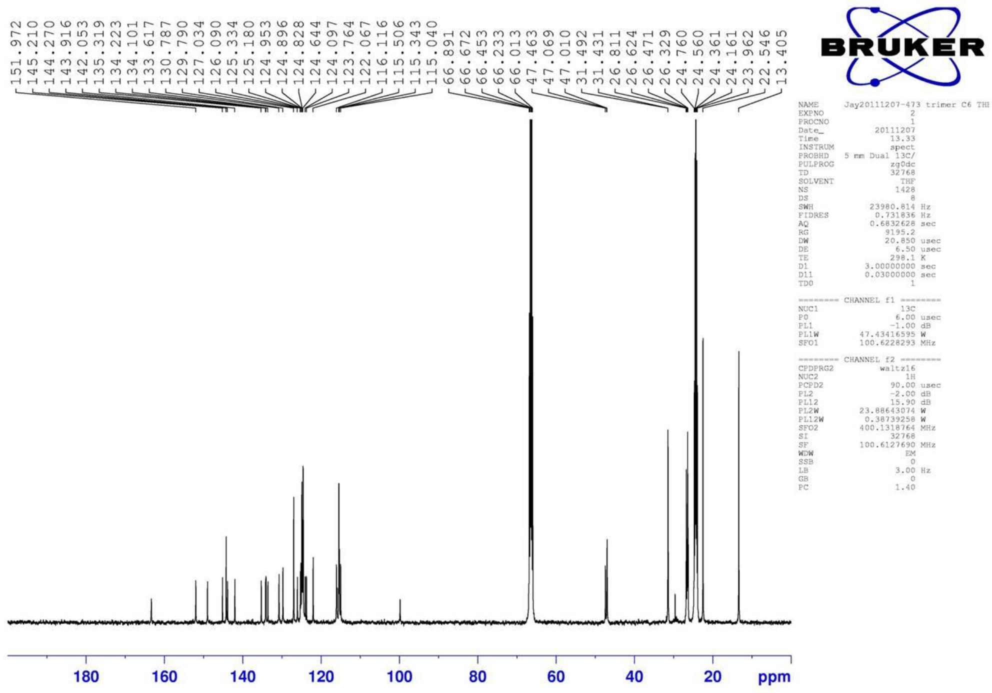
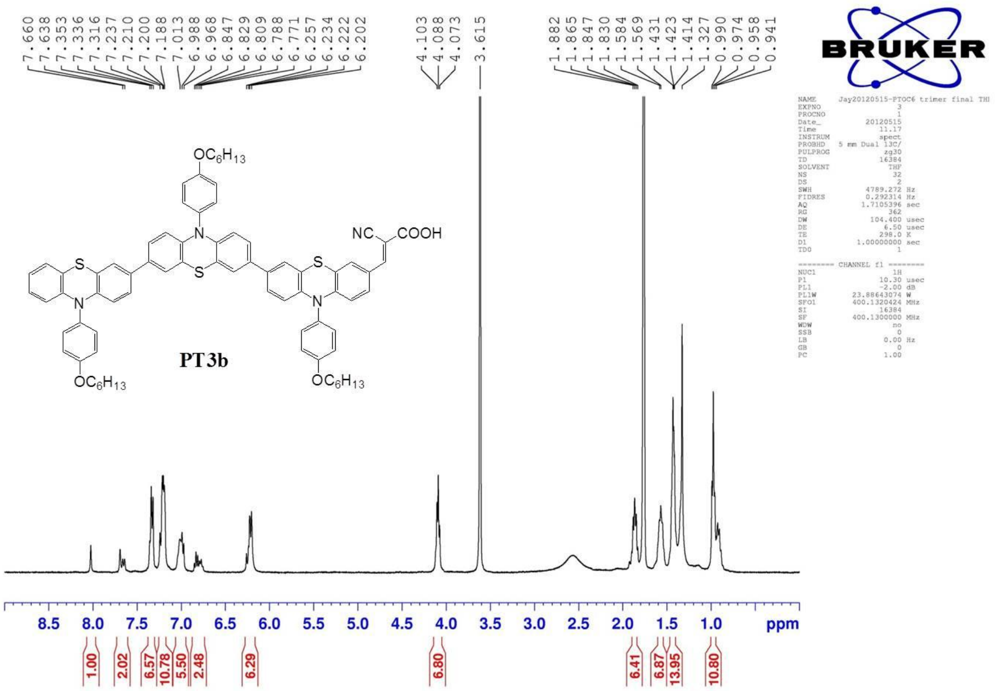


Fig. S13 ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PT3a** in THF-d_8.



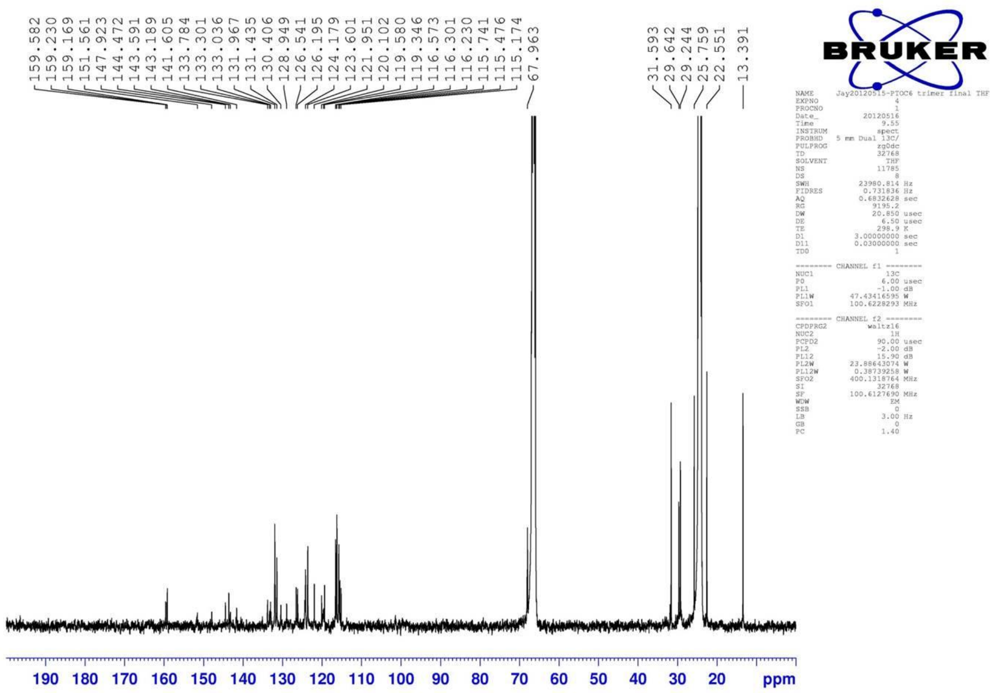


Fig. S14 ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PT3b** in THF-d_8.

2. UV/Vis spectra

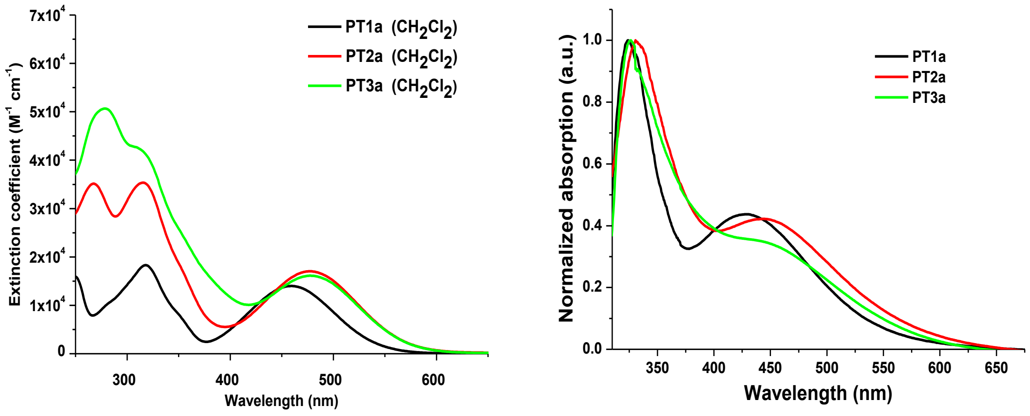


Fig. S15 The absorption spectra of organic dyes in dichloromethane (left) and on TiO_2 film (right).

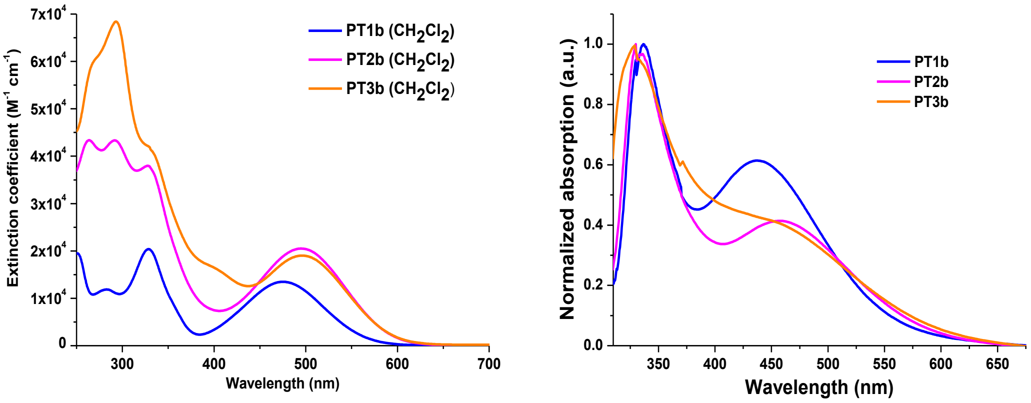


Fig. S16 The absorption spectra of organic dyes in dichloromethane (left) and on TiO_2 film (right).

3. Theoretical calculation

Table S1 Calculated *f*, HOMO/LUMO, and energy gap for dyes.

dye	*f* (oscillator strength)(S1)	HOMO/LUMO(eV)	Band gap
PT1a	0.2340	-5.47/-2.38	3.09
PT2a	0.0973	-4.87/-2.35	2.52
PT3a	0.0716	-4.88/-2.37	2.51
PT1b	0.2657	-5.25/-2.28	2.97
PT2b	0.2024	-4.81/-2.24	2.57
PT3b	0.1366	-4.64/-2.23	2.41

Table S2 Calculated Low-Lying Transition for dyes.

dye	state	excitation[a]	λ_{cal} (eV, nm)	f^{b} B3LYP/631G*	HOMO/LUMO
PT1a	S1	95.27% H→L	2.71(457)	0.2340	-5.47/-2.38
	S2	88.73% H-1→L	3.55(349)	0.2513	
	S3	85.21% H→L+1	3.95(313)	0.1333	
PT2a	S1	98.88% H→L	2.29(540)	0.0973	-4.87/ -2.35
	S2	94.42% H-1→L	2.54(488)	0.2336	
	S3	83.66% H→L+2	2.73(454)	0.2579	
PT3a	S1	93.49% H→L	2.26(549)	0.0716	-4.88/ -2.37
	S2	85.65% H-1→L	2.69(460)	0.1055	
	S3	87.91% H-2→L	3.30 (375)	0.1501	
PT1b	S1	95.43% H→L	2.60(476)	0.2657	-5.25/ -2.28
	S2	68.19% H-1→L	3.53(351)	0.1656	
	S3	68.67% H→L+1	3.71(334)	0.2913	
PT2b	S1	97.71% H→L	2.31(536)	0.2024	-4.81/ -2.24
	S2	93.99% H-1→L	2.65(468)	0.1775	
	S3	57.29% H→L+1	3.37(367)	0.2828	
PT3b	S1	95.19% H→L	2.20(564)	0.1366	-4.64/ -2.23
	S2	86.63% H-1→L	2.46(502)	0.1521	
	S3	87.72% H-2→L	2.64(469)	0.1460	

[a]H=HOMO, L=LUMO, H+1=HOMO+1, L+1=LUMO+1, and L+2=LUMO+2. [b]Oscillator strengths.

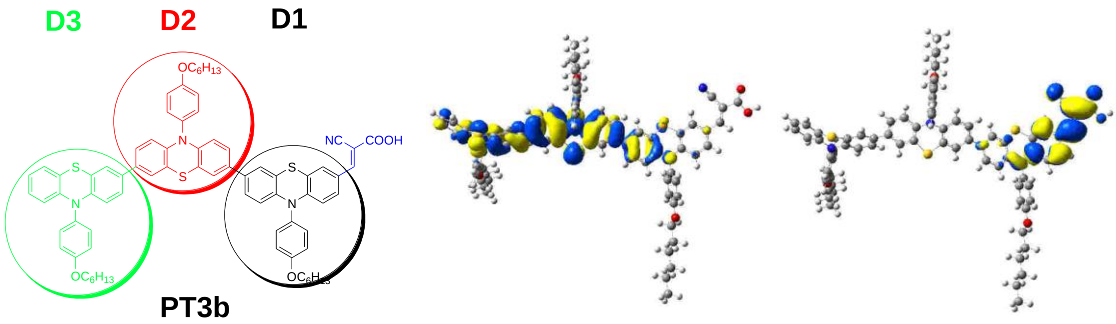


Table S3 Difference of Mulliken charges between ground state (S_0) and excited state (S_1), estimated by time dependent DFT/B3LYP model.

dye	D3	D2	D1	A
PT1a			0.55444	-0.55444
PT2a		0.75746	-0.15128	-0.60618
PT3a	0.29647	0.59981	-0.28429	-0.61199
PT1b			0.51890	-0.51890
PT2b		0.75704	-0.18077	-0.57627
PT3b	0.28154	0.60993	-0.30372	-0.58775

Difference of Mulliken charge between ground state and excited state.

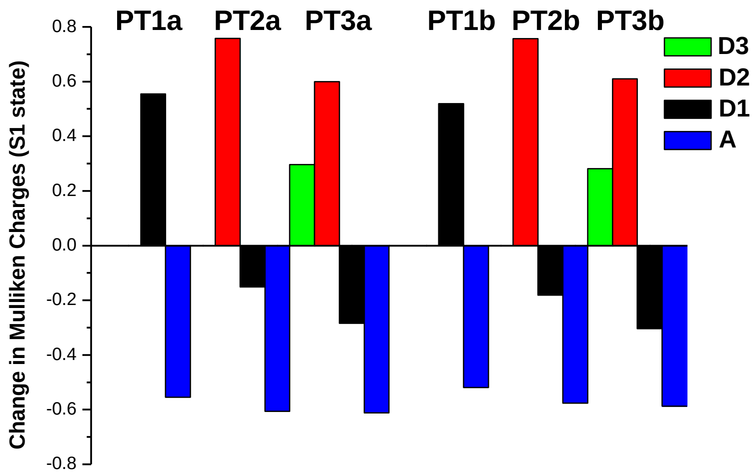


Fig. S17 Bar-chart plots foe the difference of Mulliken charge listed in Table S3.

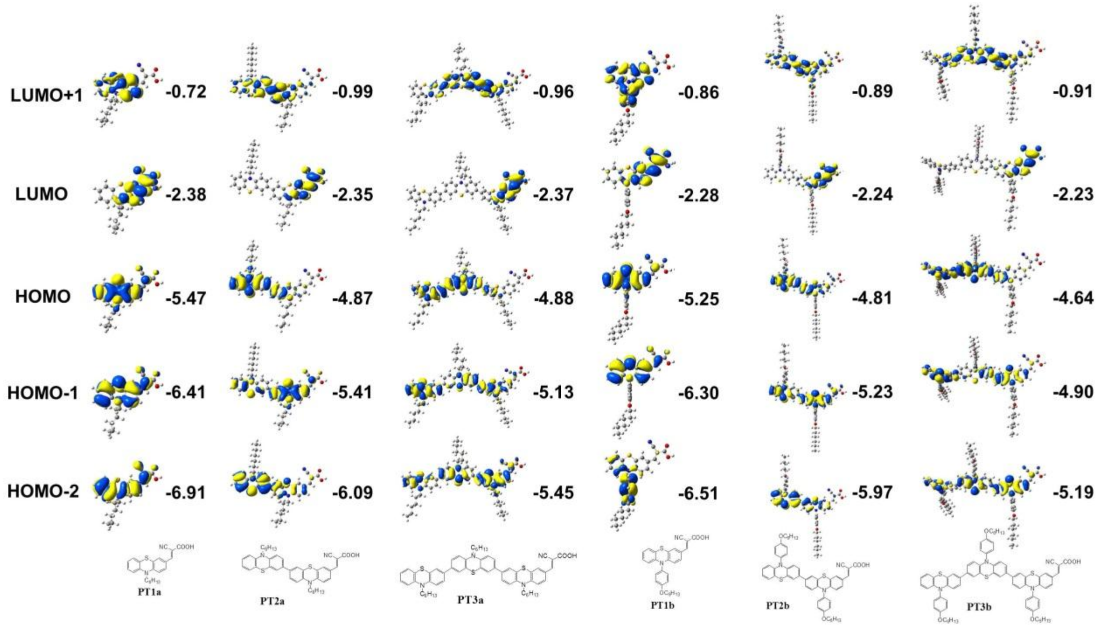


Fig. S18 Computed energy levels and molecular orbitals of oligo-phenothiazine series.

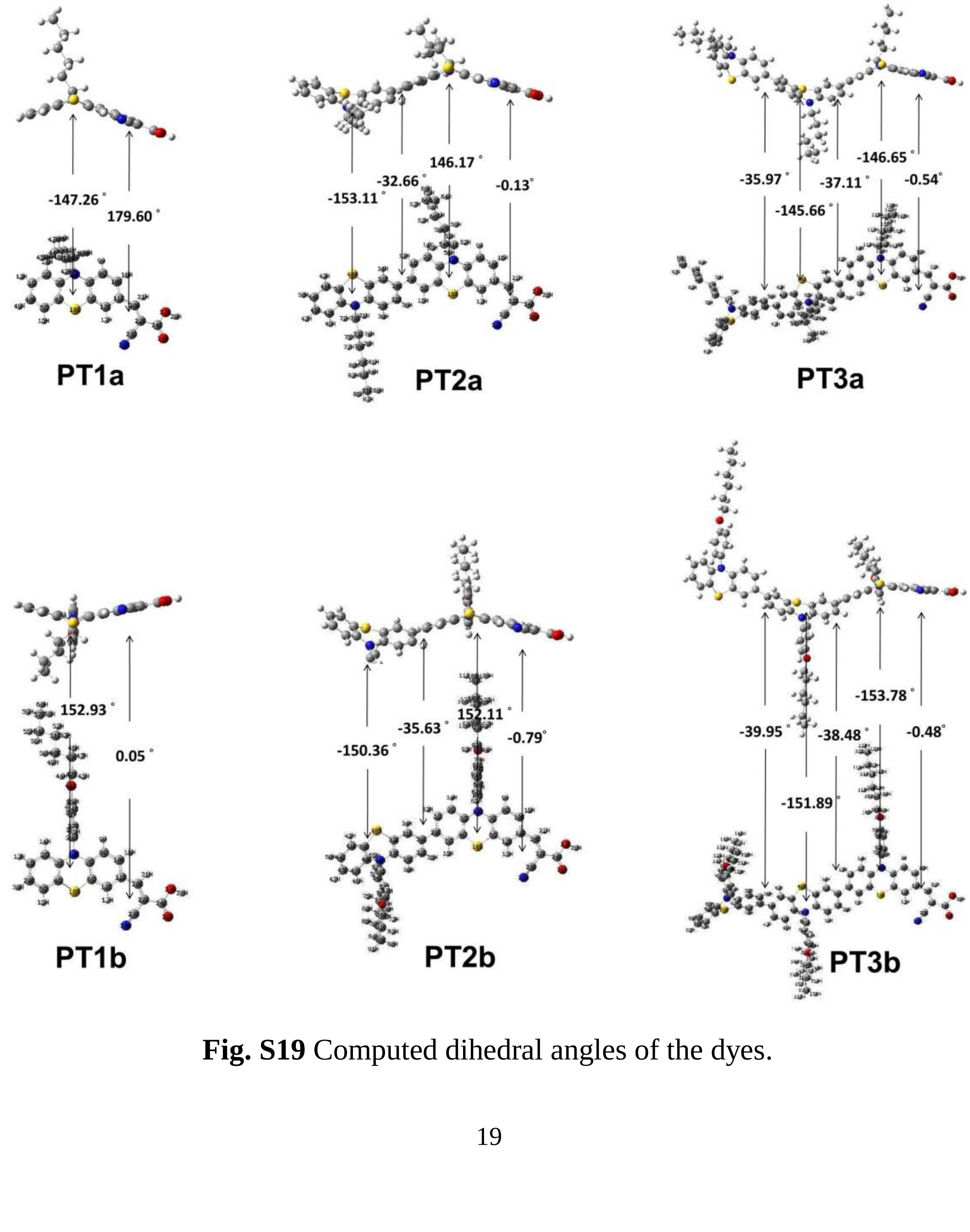


Fig. S19 Computed dihedral angles of the dyes.

4. CV spectra and HOMO-LUMO level

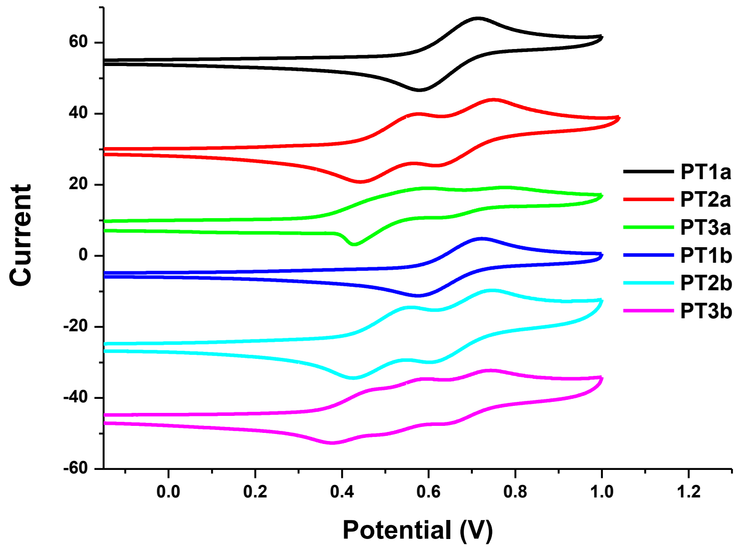


Fig. S20 Oxidative voltammograms of organic dyes.

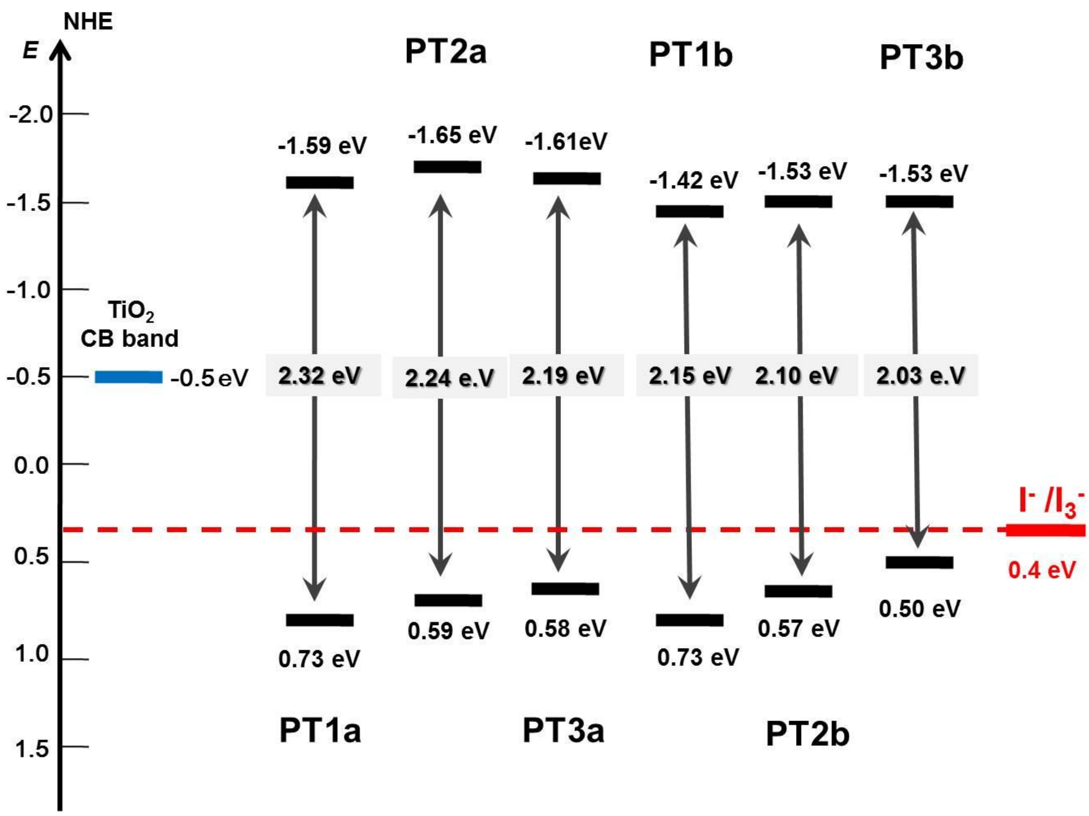


Fig. S21 HOMO-LUMO energy levels of organic dyes.

5. Performance of DSSCs devices

Table S4 Performances of DSSCs devices of **PT1a**, **PT2a**, and **PT3a** in THF and CH_2Cl_2.

Solvent system	Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η^{a}(%)
THF	**PT1a**	10.60	0.655	62.95	4.37
	PT2a	11.15	0.665	63.94	4.74
	PT3a	9.44	0.67	63.03	3.99
CH_2Cl_2	**PT1a**	10.12	0.67	62.47	4.24
	PT2a	10.31	0.675	64.23	4.47
	PT3a	8.8	0.685	63.33	3.82
MeCN+*t*-BuOH	**N719**	15.87	0.74	60.87	7.15

J_{sc} : short-current photocurrent density ; V_{oc} : open-circuit photovoltage ; FF : fill factor ; η : total power conversion efficiency. [a]Performance of DSSCs measured in a 0.25 cm^{-2} working area on a FTO (8 Ω/square) substrate. Electrolyte: LiI (0.5 M), I_2 (0.05 M), and TBP (0.5 M) in MeCN

Table S5 Performances of DSSCs devices of **PT1a, PT2a, and PT3a** in EtOH/ CH_2Cl_2 (1/9) and MeCN/*t*-BuOH (1/1).

Solvent system	Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η^{a}(%)
EtOH+CH_2Cl_2 (1/9)	**PT1a**	11.36	0.65	60.75	4.49
	PT2a	11.82	0.67	63.72	5.04
	PT3a	9.23	0.67	62.0	3.86
MeCN+*t*-BuOH (1/1)	**PT1a**	12.91	0.68	62.01	5.45
	PT2a	13.20	0.69	61.86	5.63
	PT3a	12.09	0.70	59.26	5.01
	N719	15.87	0.74	60.87	7.15

J_{sc} : short-current photocurrent density ; V_{oc} : open-circuit photovoltage ; FF : fill factor ; η : total power conversion efficiency. [a]Performance of DSSCs measured in a 0.25 cm^{-2} working area on a FTO (8 Ω/square) substrate. Electrolyte: LiI (0.5 M), I_2 (0.05 M), and TBP (0.5 M) in MeCN

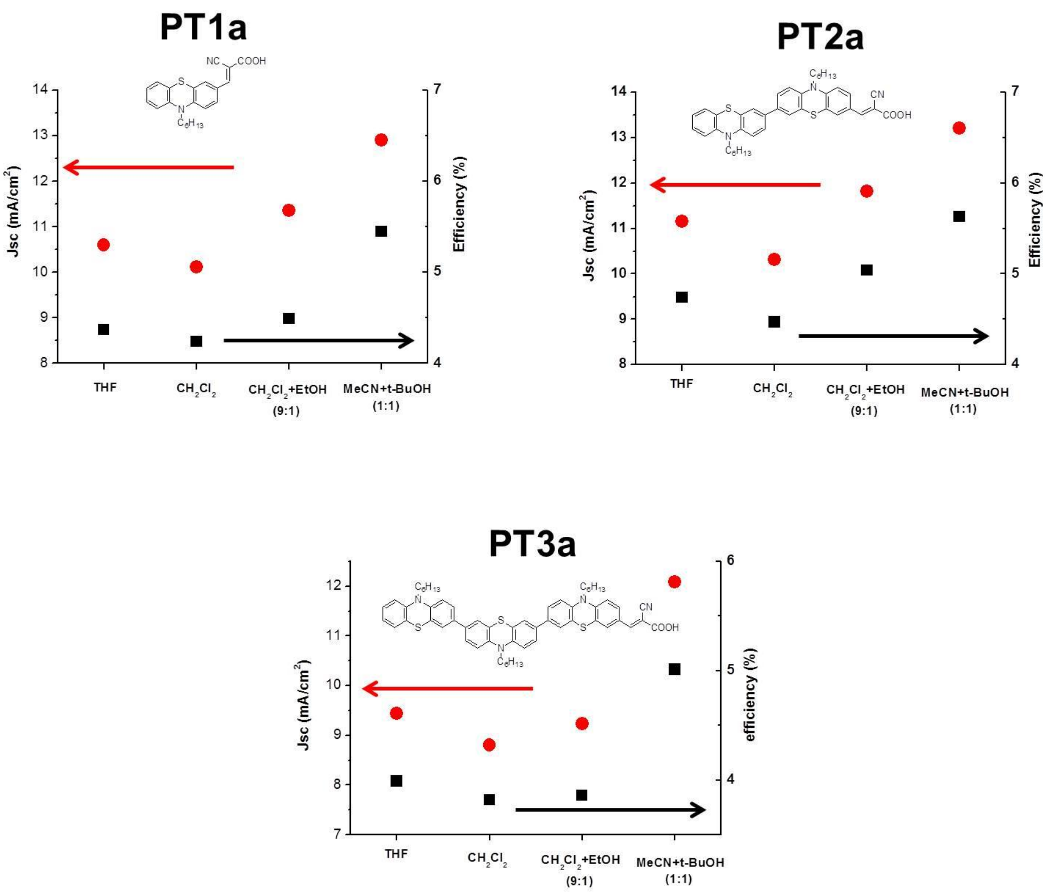


Fig. S22 Performances of DSSCs devices of **PT1a, PT2a, and PT3a** in different solvent systems.

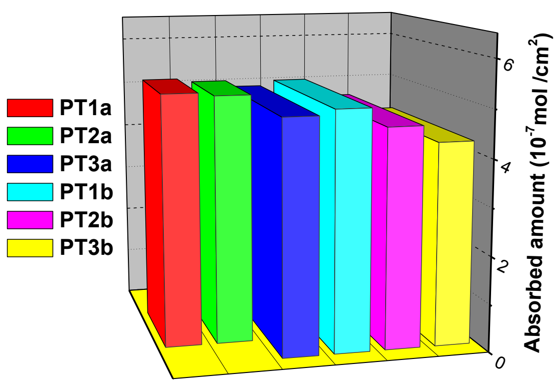


Fig. S23 Absorbed amount of organic dyes on TiO_2 film.

Table S6 Performances of DSSCs devices of **PT1a, PT2a, and PT3a** in different electrolyte system.

Solvent system	Dye	electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η^a(%)
MeCN+ *t*-BuOH (1/1)	PT1a	E1	12.91	0.68	62.01	5.45
		E2	11.03	0.76	64.84	5.43
	PT2a	E1	13.20	0.69	61.86	5.63
		E2	12.21	0.77	57.91	5.44
	PT3a	E1	12.09	0.70	59.26	5.01
		E2	10.25	0.82	60.14	5.05
	N719	E1	15.87	0.74	60.87	7.15
		E2	18.61	0.76	63.14	8.93

J_{sc} : short-current photocurrent density ; V_{oc} : open-circuit photovoltage ; FF : fill factor ; η : total power conversion efficiency. [a] Performance of DSSCs measured in a 0.25 cm^{-2} working area on a FTO (8 Ω/square) substrate. **Electrolyte 1** : LiI (0.5 M), I_2 (0.05 M), and TBP (0.5 M) in MeCN. **Electrolyte 2**: 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M tert-butylpyridine, 0.05 M lithium iodide in acetonitrile : valeronitrile (85 : 15, v/v).

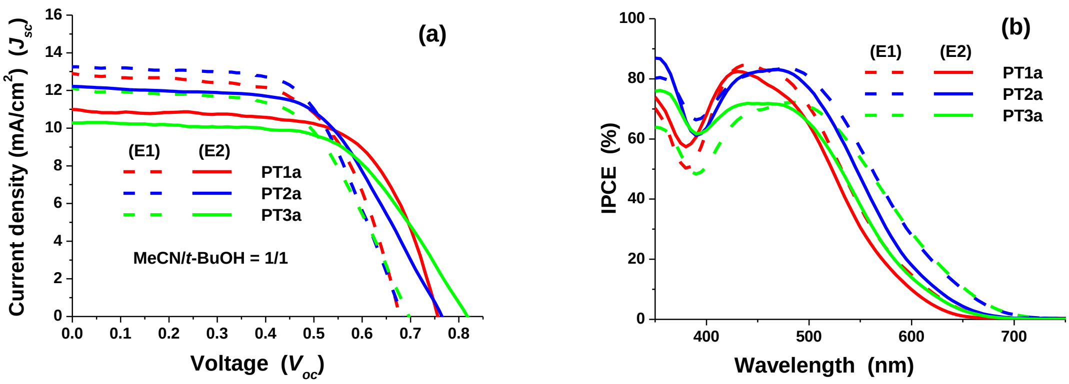


Fig. S24 Performances of DSSCs devices of **PT1a, PT2a, and PT3a** in different electrolyte systems.

Table S7 Performances of DSSCs devices of **PT1b, PT2b, and PT3b** in different electrolyte system.

Solvent system	Dye	electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η^a(%)
MeCN+ *t*-BuOH (1/1)	**PT1b**	**E1**	13.47	0.70	66.76	6.21
		E2	12.87	0.78	65.26	6.52
	PT2b	**E1**	14.48	0.71	61.26	6.30
		E2	14.00	0.82	64.30	7.38
	PT3b	**E1**	11.93	0.72	58.40	5.01
		E2	12.98	0.82	60.52	6.44
	N719	**E1**	15.87	0.74	60.87	7.15
		E2	18.61	0.76	63.14	8.93

J_{sc} : short-current photocurrent density ; V_{oc} : open-circuit photovoltage ; FF : fill factor ; η : total power conversion efficiency. [a] Performance of DSSCs measured in a 0.25 cm^{-2} working area on a FTO (8 Ω/square) substrate. **Electrolyte 1** : LiI (0.5 M), I_2 (0.05 M), and TBP (0.5 M) in MeCN. **Electrolyte 2**: 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M tert-butylpyridine, 0.05 M lithium iodide in acetonitrile : valeronitrile (85 : 15, v/v).

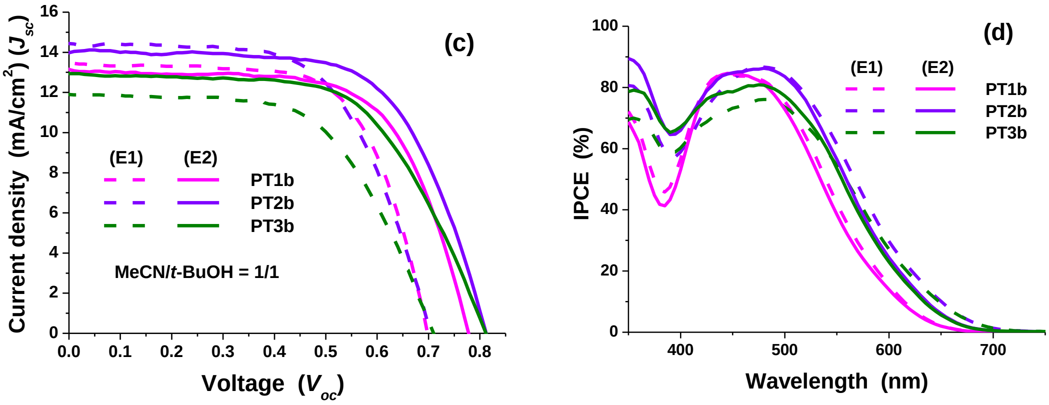


Fig. S25 Performances of DSSCs devices of **PT1b, PT2b, and PT3b** in different electrolyte systems.

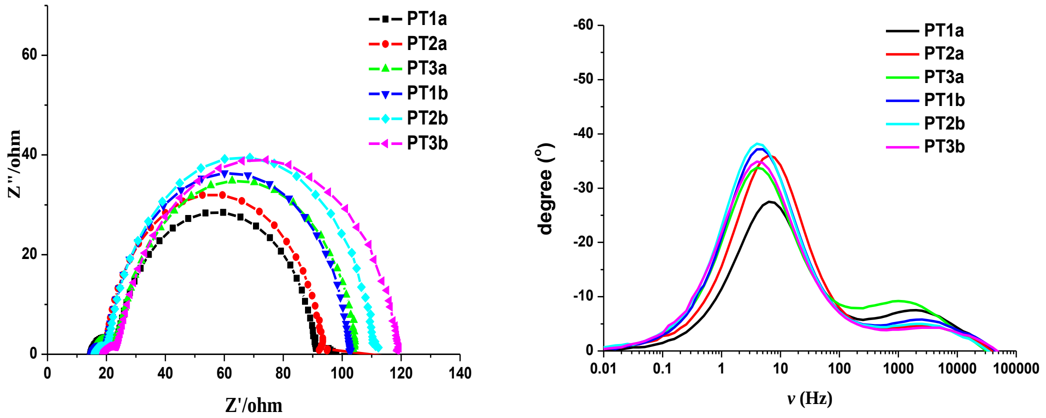


Fig. S26 EIS Nyquist plots (left) and EIS Bode phase plots (right) of dyes with electrolyte 1 (E1).

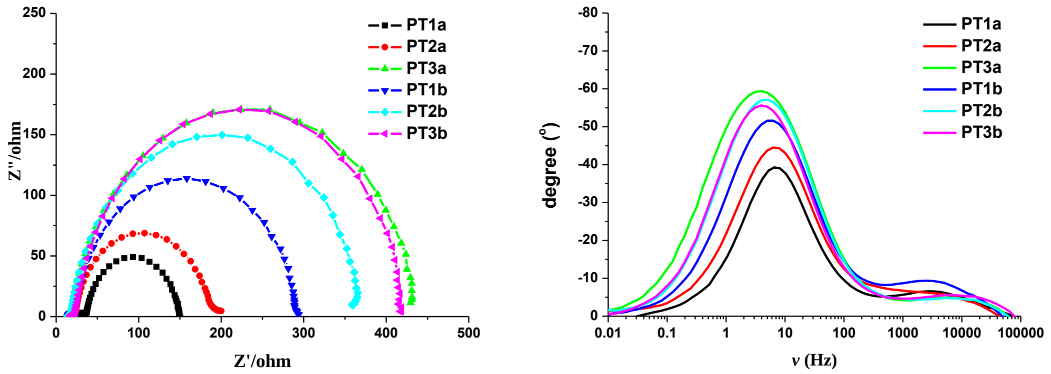


Fig. S27 EIS Nyquist plots (left) and EIS Bode phase plots (right) of dyes with electrolyte 2 (E2).

7. DCA influence

Table S8 Photovoltaic Parameters of Devices made **PT1b, PT2b, and PT3b** with and without DCA.

Dye[a]	DCA (mM)	J_{sc}(mA·cm^{-2})	V_{oc} (V)	FF	η^b (%)
PT1b	0	12.87	0.78	0.65	6.52
	10	13.03	0.80	0.67	6.98
PT2b	0	14.00	0.82	0.64	7.38
	10	14.33	0.83	0.65	7.78
PT3b	0	12.98	0.82	0.60	6.44
	10	13.33	0.83	0.62	6.87

J_{sc}: short-circuit photocurrent density; V_{oc}: open-circuit photovoltage; FF: fill factor; η: total power conversion efficiency.

[a] Concentration of dye is 3 × 10^{-4} M in MeCN/*t*-BuOH (1/1). [b] Performance of DSSC measured in a 0.25 cm^2 working area on an FTO (8 Ω /square) substrate under AM 1.5 condition. Electrolyte 2: 1.0 M, 3-dimethylimidazolium iodide (DMII), 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M tert-butylpyridine, 0.05 M lithium iodide in acetonitrile : valeronitrile (85 : 15, v/v).

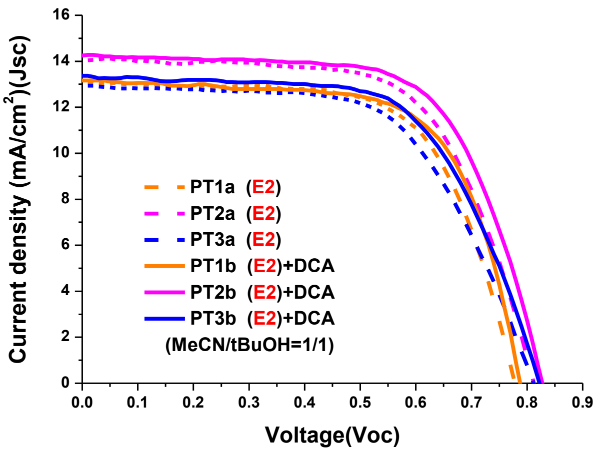


Fig. S28 Performances of DSSCs devices of **PT1b, PT2b, and PT3b** in electrolyte 2 with or without DCA.