Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Pyrazine Incorporated Panchromatic Sensitizers for Dye Sensitized Solar Cells under One Sun and Dim Light

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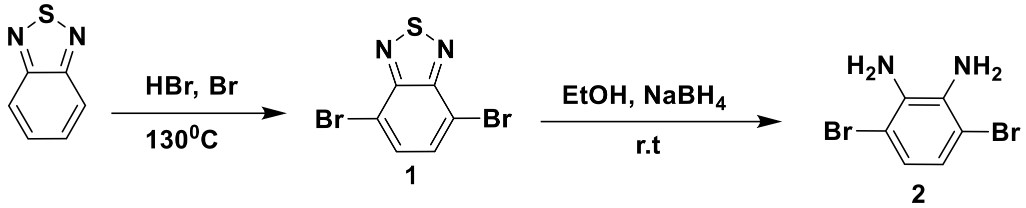
Experimental Procedures

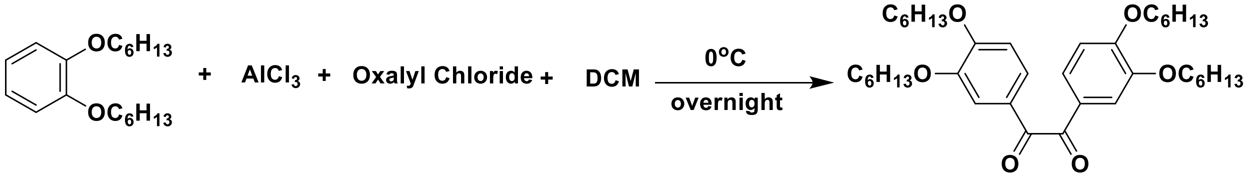
Synthesis of 3, 6-dibromobenzene-1, 2-diamine

4, 7-Dibromobenzothiadiazole (17 mmol, 5.0 g) was suspended in ethanol (250 mL) at 10 °C under nitrogen. After the slow addition of $NaBH_4$ (238 mmol, 9.0 g) the mixture was stirred at room temperature for 20 h. The solvent was evaporated and the raw product was poured into H_2O (100 mL) then extracted with DCM (200 mL). The organic layer was washed with brine solution and dried over anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography using hexane:DCM (40%) as the eluent and yielded a yellow solid (4.0 g. 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (bs, 4H), 6.82 (s, 2H).



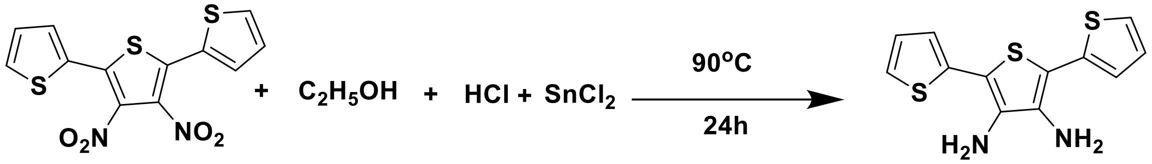
Synthesis of 1,2-bis(3,4-bis(hexyloxy)phenyl) ethane-1,2-dione

1,2-bis(Hexyloxy)benzene (18 mmol, 5.0 g), was mixed with 1,2-dichloroethane (150 mL), and stir for 30 min at 0°C under nitrogen overnight. Then 590 µL of oxalyl chloride was added slowly using syringe. The mixture was stirred at 0 °C for 10 min. $AlCl_3$ (0.96 g) was added using the solid addition flask and then stir for 0°C. The solvent was evaporated and the raw product was poured into 10% HCl (100 mL) then extracted with DCM (200 mL). The organic layer was washed with brine solution and dried over anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography using hexane: DCM (40%) as the eluent and yielded a yellow solid (3.5 g. 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91-094 (m, 12H), 1.32-1.39 (m, 14H), 1.46-1.51 (m, 10H), 4.06-4.09 (m, 8H), 6.86-6.88 (d, J = 8.4 Hz, 2H), 7.44-7.47 (dd, J = 8.4, 1.2 Hz, 2H), 7.58 (d, J = 1.2 Hz, 2H).



Synthesis of [2,2':5',2''-terthiophene]-3',4'-diamine

3',4'-Dinitro-2,2':5',2''-terthiophene (12 mmol, 3.2 g), was suspended in a mixture of ethanol (120 mL) and HCl (60 ml) at 90 °C under nitrogen for 24 h. The solvent was evaporated and KOH (25 mg in 100 mL H_2O) solution was added dropwise to the raw product then extracted with Ethyl acetate (200 mL). The organic layer was washed with solution and dried over anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by column chromatography using hexane: DCM (80%) as the eluent and yielded a yellow solid (2.0 g. 71%). ^1H NMR (400 MHz, $CDCl_3$): δ 3.50 (bs, 4H), 7.09-7.12 (m, 4H), 7.28-7.30 (m, 2H).



Synthesis of 3-(5-(7-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2,3-bis(3,4-bis(hexyloxy)phenyl)thieno[3,4-*b*]pyrazin-5-yl)thiophen-2-yl)-2-cyanoacrylic acid (**MD6**):

The synthetic procedure was similar to that of **MD4**. The crude product was purified by flash chromatography using hexane: CH_2Cl_2 (1:4 by vol.) as the eluent to afford **MD6** as a green solid (80% yield). ^1H NMR (400 MHz, THF-d_8): δ 0.85-0.93 (m, 18H), 1.23-1.45 (m, 28H), 1.70-1.83 (m, 20H), 3.68 (t, J = 6.0 Hz, 2H), 3.91-4.04 (m, 10H), 6.76-6.92 (m, 8H), 7.00-7.15 (m, 7H), 7.35-7.41 (m, 3H), 7.55-7.58 (m, 2H), 7.67-7.74 (m, 2H), ^{13}C NMR (600 MHz, THF-d_8): δ 14.67, 23.76, 30.38, 32.71, 67.29, 69.87, 114.224, 116.97, 120.886, 121.592, 123.117, 124.356, 125.150, 126,901, 127.177, 127.912, 130.081, 132.795, 133.243, 137.163, 138.489, 140.713, 141.316, 145.030, 146.774, 148.375, 149.282, 150.110, 151.845, 152.16, 153.70. MS (FAB): m/z calcd. for $C_{84}H_{102}N_4O_8S_3$ [M]: 1390.6860 found: $[M+H]^+$ 1391.6934.

*Synthesis of 2,3-bis(3,4-bis(hexyloxy)phenyl)-5,8-dibromoquinoxaline (**5a**):* 1,2-bis(3,4-bis(hexyloxy)phenyl)ethane-1,2-dione (2 mmol, 1.22 g) and 3,6-dibromobenzene-1,2-diamine (2 mmol, 0.53 g) were refluxed in a mixture of ethanol:AcOH (10:1) for 12 h. The solution was cooled and poured into the crushed ice, and the crude product was extracted with CH_2Cl_2 (100 mL x 3). The organic extracts were combined, washed with brine and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure, and the residue was purified by flash chromatography using hexane:CH_2Cl_2 (1:4 by vol.) as the eluent to afford **5a** as a yellow solid (89% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.92-0.97 (m, 12H), 1.31-1.54 (m, 24H), 1.76 (m, 4H), 1.85 (m, 4H), 3.89 (t, J = 6.6 Hz, 4H), 4.04 (t, J = 6.6 Hz, 4H), 6.84-6.89 (m, 2H), 7.27-7.32 (m, 4H), 7.87 (br, 2H). MS (FAB) m/z: 839.3 $[M+ H]^+$.

*Synthesis of 2,3-bis(3,4-bis(hexyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline (**5b**)*: 2,3-Bis(3,4-bis(hexyloxy)phenyl)-5,8-dibromoquinoxaline (1.2 mmol, 1.0 g), tributyl(thiophen-2-yl)stannane (3.6 mmol, 1.33 g) and $PdCl_2(PPh_3)_2$ (0.05 mmol, 33.6 mg) was mixed in a two neck round bottom flask under nitrogen. Then 40 mL of dry DMF was added via syringe and the mixture was stirred under nitrogen at 100 ^oC for 24 h. Reaction was monitored through TLC. After 24 h, the mixture was poured into ice water (200 mL) and extracted with DCM (100 mL x 3). The organic layer was combined, washed with brine, and dried over anhydrous $MgSO_4$. Product **5b** was obtained by flash column chromatography using hexane:CH_2Cl_2 (1:2 by vol.) as the eluent (78% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.95-1.03 (m, 12H), 1.37-1.45 (m, 16H), 1.48-1.59 (m, 8H), 1.81-1.95 (m, 8H), 4.01 (t, J = 6.5 Hz, 4H), 4.10 (t, J = 6.5 Hz, 4H), 6.90 (d, J = 8.3 Hz, 2H), 7.24 (bs, 1H), 7.32-7.38 (m, 3H), 7.53-7.58 (m, 4H), 7.91 (br, 2H), 8.15-8.18 (s, 2H). MS (FAB): m/z 847.4 $[M + H]^+$.

*Synthesis of 5-(2,3-bis(3,4-bis(hexyloxy)phenyl)-8-(thiophen-2-yl)quinoxalin-5-yl)thiophene-2-carbaldehyde (**5c**)*: The synthetic procedure was similar to **4b.** Compound **5c** was obtained as an orange solid (62% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.93-0.94 (m, 12H), 1.36-1.51 (m, 24H), 1.73-1.88 (m, 8H), 3.90 (t, J = 6.4 Hz, 2H), 3.97-4.05 (m, 6H), 6.71-6.78 (m, 2H), 7.00-7.05 (m, 2H), 7.16-7.18 (m, 1H), 735-7.59 (m, 5H), 7.60-7.61 (m, 3H), 9.80 (s, 1H). MS (FAB): 875.4 [M+ H]$^+$.

*Synthesis of 5-(2,3-bis(3,4-bis(hexyloxy)phenyl)-8-(5-bromothiophen-2-yl)quinoxalin-5-yl)thiophene-2-carbaldehyde (**5d**)*: The synthetic procedure was similar to **4c**. and the product was purified by flash column chromatography using hexane:CH_2Cl_2 (1:4 by vol.) as the eluent. Compound **5d** was obtained as a red solid (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88-0.96 (m, 12H), 1.31-1.39 (m, 16), 1.47-1.56 (m, 8H), 1.81-1.89 (m, 6H), 4.00-4.10 (m, 8H), 6.75 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 4.0 Hz, 1H), 7.03 (dd, J = 2.0; 6.5 Hz, 1H), 7.13 (dd, J = 1.8; 6.4 Hz, 1H), 7.29 (d, J = 4.0 Hz, 1H), 7.51-7.52 (m, 1H), 7.56-7.58 (m, 2H), 7.61 (d, J = 4.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 9.88 (s, 1H). MS (FAB): 953.4 [M+ H]$^+$.

*Synthesis of 5-(2,3-bis(3,4-bis(hexyloxy)phenyl)-8-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)quinoxalin-5-yl)thiophene-2-carbaldehyde (**5e**)*: The synthetic procedure was similar to that of **4d**. The crude product was purified by flash chromatography using hexane:CH_2Cl_2 (1:4 by vol.) as the eluent to afford **5e** as a brown solid (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88-0.99 (m, 12H), 1.35-1.43 (m, 16), 1.48-1.58 (m, 6H), 1.67-1.73 (m, 4H), 1.82-1.92 (m, 6H), 3.94-3.99 (m, 2H), 4.02-4.13 (m, 6H), 6.82-6.87 (m, 2H), 7.08-7.14 (m, 4H), 7.16-7.19 (m, 4H), 7.20-7.25 (m, 2H), 7.27-7.34 (m, 5H), 7.55-7.62 (m, 4H), 7.74-7.77 (m, 1H), 7.79-7.84 (m, 2H), 8.0-8.08 (m, 2H), 9.97 (m, 1H). MS (FAB): 1117.76 [M+ H]$^+$.

*Synthesis of 5-(8-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2,3-bis(3,4-bis(hexyloxy)phenyl)quinoxalin-5-yl)thiophene-2-carbaldehyde (**5f**)*:

The synthetic procedure was similar to that of **4d** except that 4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-*N*-(4-(tributylstannyl)phenyl)aniline was used instead of *N*,*N*-diphenyl-4-

(tributylstannyl)aniline. The crude product was purified by flash chromatography using hexane:CH_2Cl_2 (1:3 by vol.) as the eluent to afford **5f** as a brown solid (87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88-0.90 (m, 18H), 1.23-1.54 (m, 36H), 1.64-1.68 (m, 2H), 1.73-1.83 (m, 10H), 3.92 (t, J = 6.0 Hz, 6H), 4.00-4.04 (m, 6H), 6.77-6.83 (m, 6H), 6.90 (d, J = 7.6 Hz, 2H), 7.04 (d, J = 8 Hz, 4H), 7.17-7.23 (m, 3H), 7.44-7.47 (d, J = 8.4 Hz), 7.55 (bs, 2H), 7.75-7.76 (m 1H), 7.82 (br, 2H), 8.03-8.11 (m, 2H), 9.94 (s, 1H). HRMS (FAB): m/z calculated for $C_{83}H_{103}N_3O_7S_2$ [M] 1317.7237; found $[M+ H]^+$.1318.7302.

*Synthesis of 3-(5-(2,3-bis(3,4-bis(hexyloxy)phenyl)-8-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)quinoxalin-5-yl)thiophen-2-yl)-2-cyanoacrylic acid (**MD5**)*: The synthetic procedure was similar to that of **MD4**. The crude product was purified by flash chromatography using 1% acetic acid in CH_2Cl_2 as the eluent to afford **MD5** as a dark brown solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-1.03 (m, 12H), 1.27-1.53 (m, 22H), 1.56-1.63 (m, 2H), 1.64-1.73 (m, 4H), 1.79-1.88 (m, 2H), 1.89-1.98 (m, 2H), 3.70 (t, J = 6.5 Hz, 2H), 3.93 (t, J = 6.5 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 4.17 (t, J = 6.5 Hz, 2H), 6.77 (d, J = 8.3 Hz, 1H), 6.94 (br, 1H), 7.01-7.17 (m, 10H), 7.22 (d, J = 8.3 Hz, 1H), 7.26-7.33 (m, 5H), 7.39-7.57 (m, 5H), 7.61-7.71 (m, 2H), 7.81 (d, J = 7.5 Hz, 1H), 8.25 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ. 14.02, 22.64,25.71, 25.78, 29.07, 29.23, 29.29, 31.55, 31.58, 31.63, 31.68, 69.33, 112.67, 113.97, 115.76, 116.12, 122.19, 123.29, 123.81, 124.11, 124.71, 125.17, 126.52, 126.71, 127.41, 128.13, 128.45, 129.37, 130.59, 131.16, 133.27, 1136.38, 136.72, 136.84, 138.00, 147.44, 147.79, 148.11, 148.22, 149.05, 150.08, 150.33, 150.65, 151.48, 152.07 HRMS (FAB): m/z calculated for $C_{74}H_{80}N_4O_6S_2$ [M] 1184.5519; found $[M + H]^+$ 1185.5596.

*Synthesis of 3-(5-(7-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2,3-bis(3,4-bis(hexyloxy)phenyl)thieno[3,4-b]pyrazin-5-yl)thiophen-2-yl)-2-cyanoacrylic acid (**MD6**):* The synthetic procedure was similar to that of **MD4**. The crude product was purified by flash chromatography using hexane: CH_2Cl_2 (1:4 by vol.) as the eluent to afford **MD6** as a green solid (80% yield). ^{1}H NMR (400 MHz, THF-d_8): δ 0.85-0.93 (m, 18H), 1.23-1.45 (m, 28H), 1.70-1.83 (m, 20H), 3.68 (t, J = 6.0 Hz, 2H), 3.91-4.04 (m, 10H), 6.76-6.92 (m, 8H), 7.00-7.15 (m, 7H), 7.35-7.41 (m, 3H), 7.55-7.58 (m, 2H), 7.67-7.74 (m, 2H), ^{13}C NMR (600 MHz, THF-d_8): δ 14.67, 23.76, 30.38, 32.71, 67.29, 69.87, 114.224, 116.97, 120.886, 121.592, 123.117, 124.356, 125.150, 126,901, 127.177, 127.912, 130.081, 132.795, 133.243, 137.163, 138.489, 140.713, 141.316, 145.030, 146.774, 148.375, 149.282, 150.110, 151.845, 152.16, 153.70. MS (FAB): m/z calcd. for $C_{84}H_{102}N_4O_8S_3$ [M]: 1390.6860 found: $[M+H]^+$ 1391.6934.

*Synthesis of 3-(5-(8-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2,3-bis(3,4-bis(hexyloxy)phenyl)quinoxalin-5-yl)thiophen-2-yl)-2-cyanoacrylic acid (**MD7**):* The synthetic procedure was similar to that of **MD5**. The crude product was purified by flash chromatography using 1% acetic acid in CH_2Cl_2 as the eluent to afford **MD7** as a dark brown solid (95% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91-0.93 (m, 18H), 1.31-1.37 (m, 30H), 1.50-1.52 (m, 8H), 1.65-1.69 (m, 4H), 1.72-1.80 (m, 6H), 3.78 (t, J = 6.5 Hz, 2H), 3.93-4.05 (m, 10H), 6.84-6.87 (m, 7H), 7.04 (d, J = 7.6 Hz, 5H), 7.19-7.23 (m, 2H), 7.28 (bs, 1H), 7.50-7.52 (d, J = 8 Hz, 2H), 7.61 (bs, 1H), 7.70-7.72 (d, J = 8 Hz, 1H), 7.92-7.98 (m, 3H), 8.13-8.30 (m, J = 7.2 Hz, 18.0 Hz, 2H), 8.33 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ. 14.60, 23.71, 25.10, 25.30, 25.50, 25.70, 25.90, 26.94, 30.52, 32.73, 32.78, 67.15, 67.37, 67.59, 67.81, 68.03, 113.80, 114.81, 116.27, 117.15, 117.26, 121.27, 122.60, 124.84, 125.29, 126.24, 127.27, 127.77, 127.94, 128.41, 129.22, 129.61, 131.98, 132.55, 134.11, 137.04, 137.41, 137.90, 139.72, 141.58, 146.67, 149.03, 149.65, 149.74, 150.40, 151.77, 151.88, 152.65, 153.16, 157.13, 164.68. HRMS (FAB): m/z calculated for $C_{86}H_{104}N_4O_8S_2$ [M] 1384.7296; found $[M+H]^+$ 1385.7382.

Table S1 Calculated excitation energies for **MD4** in THF solution.

N_States	*E* (ev)	WL (nm)	*f*	Major Contributions
1	1.97	627	1.0799	H→L (83%), H-1→L (12%)
2	2.91	425	1.3177	H-2→L (28%), H-1→L (36%), H→L+1 (14%)
3	3.09	400	0.3091	H-1→L+1 (20%), H→L+1 (54%)
4	3.21	385	0.1392	H-2→L (52%), H-1→L (22%)
5	3.45	358	0.0100	H-14→L (23%), H-10→L (12%)
6	3.64	340	0.0193	H→L+2 (75%)
7	3.82	324	0.6272	H-3→L (66%)
8	3.94	314	0.1476	H-5→L (11%), H-4→L (45%)
9	4.13	299	0.0334	H-12→L (20%), H-2→L+1 (20%)
10	4.14	298	0.0691	H-12→L (11%), H-5→L (42%)

WL: wavelength; f: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S2 Calculated excitation energies for **MD5** in THF solution.

N_States	*E* (eV)	WL (nm)	f	Major Contributions
1	2.67	464	1.4533	H-1→L (33%), H→L (52%)
2	3.29	376	0.8256	H-4→L (14%), H-2→L (32%)
3	3.56	348	0.0038	H-2→L (31%), H-1→L (20%)
4	3.61	342	0.1107	H-10→L+1 (13%), H-1→L+1 (20%)
5	3.74	331	0.0231	H-10→L (13%), H-1→L+1 (16%)
6	3.89	318	0.6401	H→L (16%), H→L+3 (53%)
7	4.13	300	0.1292	H-1→L+2 (23%), H→L+2 (23%)
8	4.16	297	0.0943	H-3→L (29%), H-2→L+2 (14%)
9	4.21	294	0.534	H-4→L (25%), H-3→L (10%)
10	4.24	292	0.0236	H→L+4 (76%), H-1→L+4 (8%)

WL: wavelength; f: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S3 Calculated excitation energies for **MD6** in THF solution.

N_states	*E* (eV)	WL (nm)	*f*	Major Contributions
1	1.93	642	1.1273	H-1→L (19%), H→L (75%)
2	2.83	437	1.2425	H-2→L (29%), H-1→L (38%)
3	3.03	408	0.3279	H-1→L+1 (24%), H→L+1 (38%)
4	3.12	396	0.0285	H-2→L (51%), H-1→L (12%), H→L+1 (14%)
5	3.43	360	0.0220	H-12→L(44%), H-12→L+1 (12%)
6	3.58	345	0.7189	H→L+2 (72%)
7	3.76	329	0.1233	H-4→L (30%), H-3→L (36%)
8	3.84	322	0.0060	H-4→L (37%), H-3→L (27%)
9	4.04	306	0.0599	H-6→L (33%), H→L+4 (22%)
10	4.05	305	0.0225	H-6→L (20%), H-1→L+4 (14%)

WL: wavelength; f: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S4 Calculated excitation energies for **MD7** in THF solution.

N_States	*E* (eV)	WL (nm)	*f*	Composition
1	2.60	476	1.4940	H-1→L (32%), H→L (51%)
2	3.23	382	0.8214	H-2→L (20%), H-1→L (18%)
3	3.51	352	0.0352	H-2→L (23%), H-1→L (20%)
4	3.56	347	0.0451	H-1→L+1 (21%), H→L+1 (21%)
5	3.71	334	0.1506	H-12→L (14%), H-12→L+1 (14%)
6	3.79	326	0.6569	H-4→L (11%), H-3→L (10%)
7	4.06	305	0.1080	H→L+4 (78%)
8	4.08	303	0.0307	H-1→L+2 (17%), H→L+2 (19%)
9	4.14	299	0.0301	H-3→L (19%), H-2→L+1 (14%)
10	4.18	292	0.1594	H-14→L (13%), H-3→L (11%)

WL: wavelength; f: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S5 Molecules with (**MD4**−**MD7**) and without (**MD4'**−**MD7'**) OMe group (CAM-B3LYP in THF).

dye	HOMO	LUMO	Wave length (λ)	*f*
	With/With out	With/With out	With/With out	With/With out
MD4/MD4'	-6.24/-6.33	-2.44/-2.29	627/567	1.0799/1.0107
MD5/MD5'	-6.45/-6.46	-2.15/-1.97	464/430	1.4533/1.4428
MD6/MD6'	-6.08/-6.16	-2.41/-2.28	642/577	1.1273/1.0372
MD7/MD7'	-6.21/-6.22	-2.12/-1.96	476/438	1.4940/1.4206

Table S6 Calculated Mulliken charges difference (Δq) between the excited-state and ground states for different segments of the **MD** dyes calculated from the CAM-B3LYP/6-311G for the S_1 and S_2 states.

dye	State	f^{c}	Δ(Mulliken charge),^{d} |e| (Δq)		$f \times |(\Delta q)|$	dye	State	f^{c}	Δ(Mulliken charge),^{d} |e| (Δq)		$f \times |(\Delta q)|^{a}$
MD4	S_1	1.08	D	0.09		**MD5**	S_1	1.45	D	0.14	
			Th-L	0.08					Th-L	0.02	
			Th-R	-0.01					Th-R	-0.04	
			A'	-0.11					A'	-0.11	
			A	-0.06	0.06				A	-0.11	0.15
	S_2	1.32	D	0.13			S_2	0.83	D	0.11	
			Th-L	0.00					Th-L	0.00	
			Th-R	-0.05					Th-R	-0.02	
			A'	-0.02					A'	0.01	
			A	-0.11	0.14				A	-0.11	0.10
MD6	S_1	1.13	D	0.12		**MD7**	S_1	1.49	D	0.17	
			Th-L	0.08					Th-L	0.00	
			Th-R	-0.02					Th-R	-0.01	
			A'	-0.11					A'	-0.04	
			A	-0.06	0.07				A	-0.12	0.17
	S_2	1.24	D	0.20			S_2	0.82	D	0.17	
			Th-L	-0.02					Th-L	0.00	
			Th-R	-0.05					Th-R	-0.01	
			A'	-0.01					A'	-0.04	
			A	-0.11	0.14				A	-0.12	0.10

[a]Oscillator strength; [b]The difference of the Mulliken charge between the ground state and excited state;

[c] The product of the oscillator strength and the Mulliken charge of the acceptor A.

Table S7 Photovoltaic parameters of **MD** dyes measured using T5 fluorescent light[a]

dye	illuminance Lux	irradiance mW cm^{-2}	V_{OC} mV	J_{SC} μA cm^{-2}	*FF* %	η %
MD4	300	0.09	499.16 ± 2.61	15.49 ± 0.51	75.18 ± 0.91	6.39 ± 0.13
	600	0.18	516.03 ± 2.57	29.95 ± 0.13	75.58 ± 0.31	6.67 ± 0.11
	900	0.27	530.11 ± 0.69	44.82 ± 0.79	76.35 ± 0.13	6.81 ± 0.19
	1200	0.35	536.02 ± 1.13	60.56 ± 0.41	77.33 ± 0.12	7.22 ± 0.13
	2400	0.7	555.92 ± 0.76	124.01 ± 0.75	77.44 ± 0.44	7.70 ± 0.00
	3600	1.05	565.74 ± 0.54	185.96 ± 0.08	76.98 ± 0.06	7.90 ± 0.05
	4800	1.35	572.82 ± 1.09	246.66 ± 0.48	77.18 ± 0.49	8.27 ± 0.03
	6000	1.7	582.26 ± 5.09	315.06 ± 0.00	76.63 ± 0.06	8.62 ± 0.16
MD5	300	0.09	543.26 ± 18.25	33.47 ± 0.66	77.24 ± 2.01	15.10 ± 0.67
	600	0.18	568.20 ± 15.53	67.95 ± 1.07	77.73 ± 1.73	16.49 ± 0.40
	900	0.27	586.23 ± 16.40	104.61 ± 1.96	78.04 ± 1.67	17.38 ± 0.38
	1200	0.35	596.48 ± 15.81	141.00 ± 1.43	78.33 ± 1.55	18.25 ± 0.39
	2400	0.7	621.24 ± 14.70	288.43 ± 5.35	79.02 ± 1.56	19.85 ± 0.46
	3600	1.05	634.41 ± 12.04	446.74 ± 10.13	79.01 ± 1.30	21.23 ± 0.18
	4800	1.35	646.99 ± 13.64	599.87 ± 17.55	79.11 ± 1.36	22.50 ± 0.35
	6000	1.7	651.16 ± 10.24	762.13 ± 26.12	79.01 ± 1.27	23.17 ± 0.22
MD6	300	0.09	542.85 ± 7.68	26.87 ± 0.81	76.21 ± 0.94	12.08 ± 0.02
	600	0.18	561.95 ± 8.00	53.46 ± 1.19	77.05 ± 0.68	12.79 ± 0.05

	900	0.27	575.60 ± 9.52	80.72 ± 1.14	77.76 ± 1.01	13.24 ± 0.11
	1200	0.35	588.76 ± 7.88	108.20 ± 1.36	77.72 ± 0.84	13.83 ± 0.17
	2400	0.7	609.51 ± 3.90	218.65 ± 2.31	77.57 ± 0.80	14.72 ± 0.18
	3600	1.05	620.36 ± 8.45	333.43 ± 3.21	77.77 ± 0.84	15.48 ± 0.12
	4800	1.35	628.18 ± 4.18	442.06 ± 3.97	77.56 ± 0.85	16.08 ± 0.18
	6000	1.7	634.48 ± 8.30	562.20 ± 1.51	77.40 ± 0.82	16.86 ± 0.23
MD7	300	0.09	572.67 ± 3.79	40.92 ± 1.76	75.85 ± 0.68	18.95 ± 0.69
	600	0.18	596.77 ± 4.40	81.80 ± 2.15	76.59 ± 0.77	20.16 ± 1.10
	900	0.27	611.89 ± 4.22	124.33 ± 3.47	76.83 ± 0.83	21.10 ± 1.20
	1200	0.35	623.66 ± 6.20	165.84 ± 5.09	76.95 ± 0.81	21.74 ± 1.21
	2400	0.7	645.48 ± 5.56	341.84 ± 11.00	76.84 ± 0.40	23.43 ± 1.27
	3600	1.05	660.89 ± 4.51	531.80 ± 17.60	76.61 ± 0.58	24.78 ± 1.08
	4800	1.35	668.51 ± 4.52	725.66 ± 27.27	76.60 ± 0.32	25.81 ± 1.14
	6000	1.7	676.32 ± 6.32	913.69 ± 37.34	76.42 ± 0.38	27.17 ± 1.44
N719	300	0.09	550.53 ± 12.34	41.48 ± 0.51	75.34 ± 1.17	19.02 ± 0.70
	600	0.18	582.94 ± 13.91	82.17 ± 2.50	75.72 ± 1.50	20.23 ± 0.89
	900	0.27	597.55 ± 14.28	126.06 ± 4.43	75.72 ± 2.27	20.94 ± 1.06
	1200	0.35	611.28 ± 16.83	168.65 ± 5.03	75.79 ± 2.47	21.70 ± 0.94
	2400	0.7	637.91 ± 18.31	344.82 ± 3.87	760 ± 2.04	23.53 ± 0.77
	3600	1.05	653.08 ± 22.24	529.36 ± 3.62	76.19 ± 2.19	25.02 ± 0.14
	4800	1.35	666.86 ± 22.83	720.24 ± 21.00	76.26 ± 2.07	26.32 ± 0.18
	6000	1.7	676.37 ± 24.38	923.38 ± 27.29	75.85 ± 1.98	27.64 ± 0.54

[a] V_{OC}: open-circuit voltage; J_{SC}: short-circuit current; *FF*: fill factor; *PCE*: power-conversion efficiency. The data are based on five measurements. Experiments were conducted by using TiO_2 photoelectrodes, soaked with dyes and CDCA (1 mM), with approximately 12 μm thickness and 0.16 cm^2 working area on fluorine-doped tin oxide substrates.

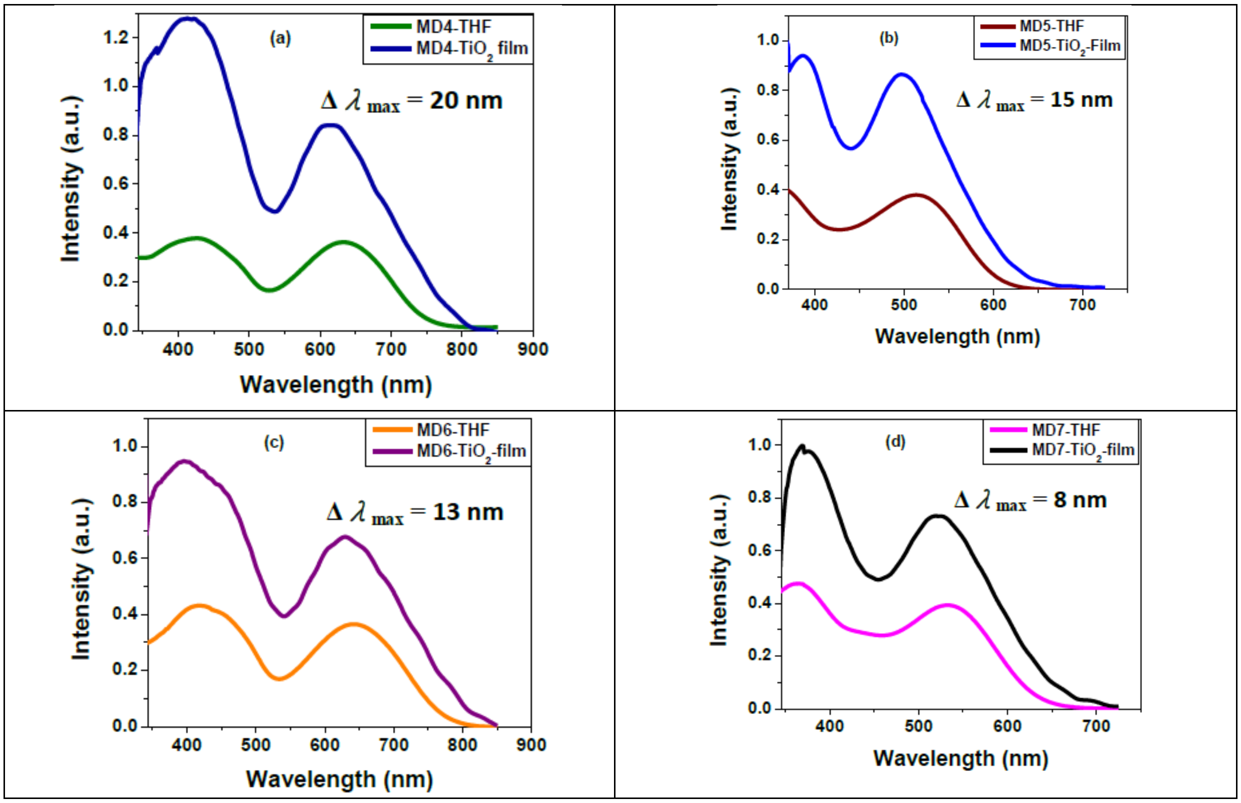


Fig. S1 Comparison of the solution (in THF) and film spectra for **MD** dyes.

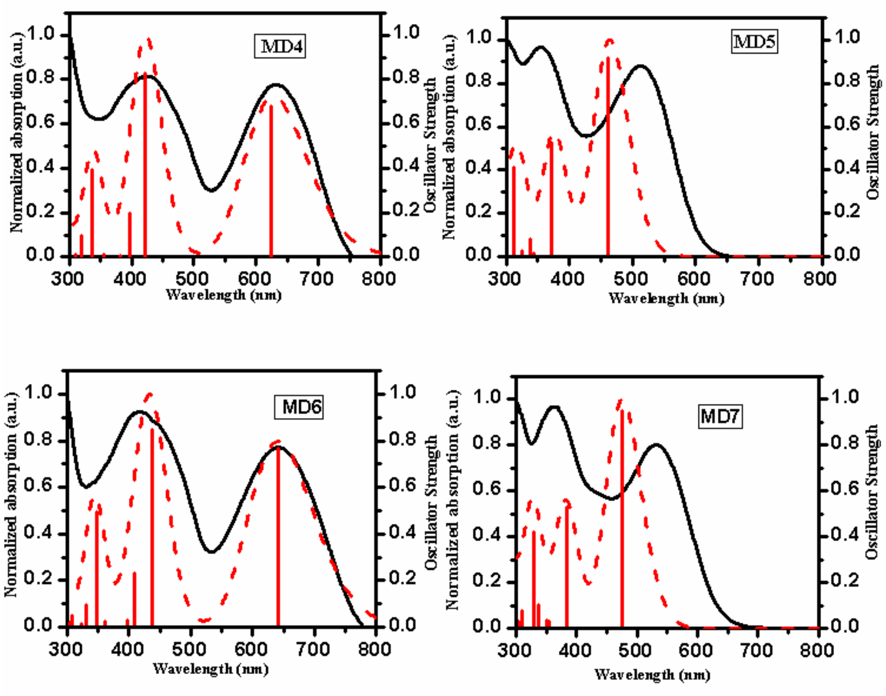
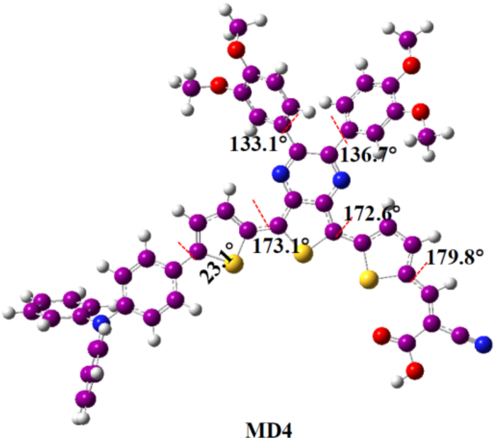
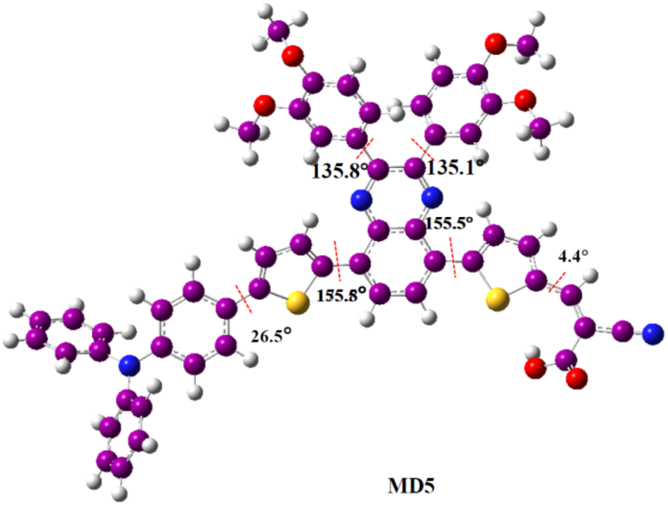


Fig. S2 Experimental (black lines) and calculated (red lines) UV-Vis absorption spectra of the **MD** dyes in THF solution. Red vertical lines represent the calculated singlet excitation energies in GaussSum 2.2.5.



MD4



MD5

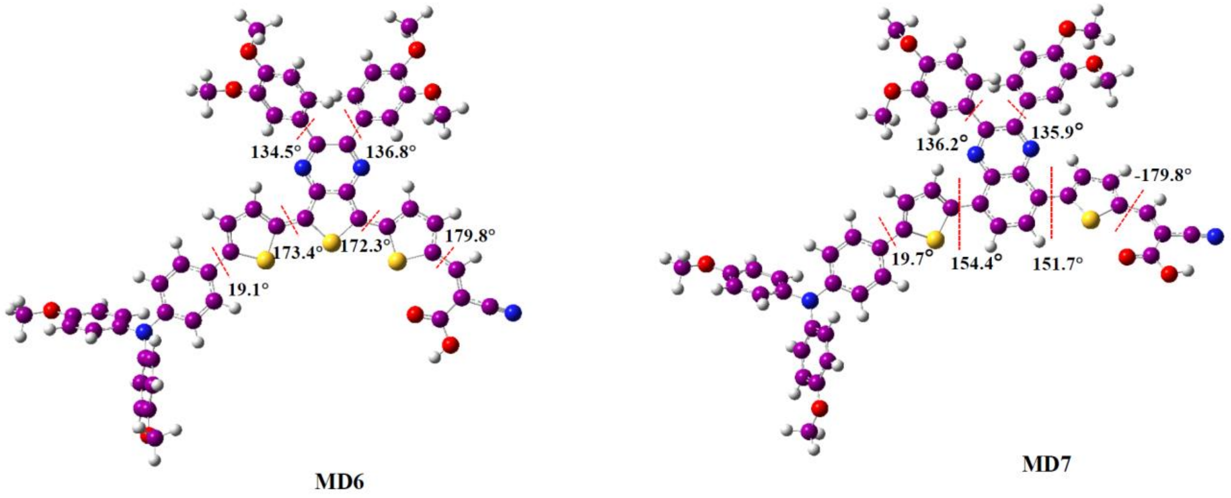
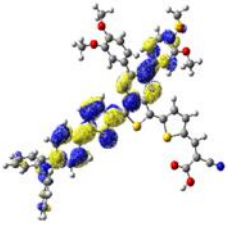
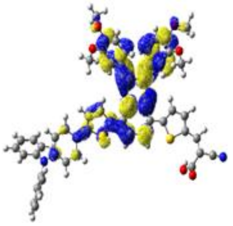
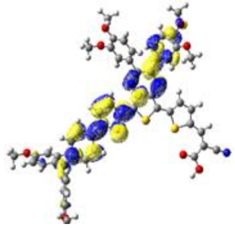
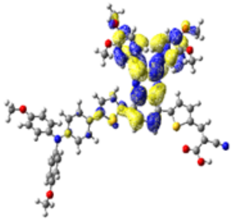
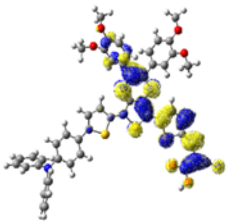
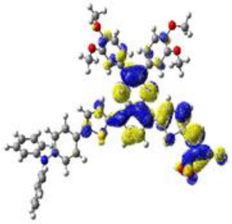
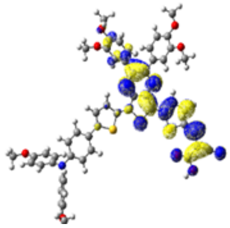
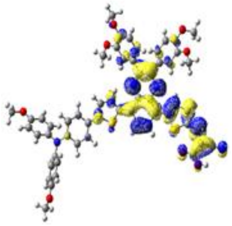
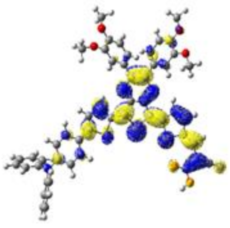
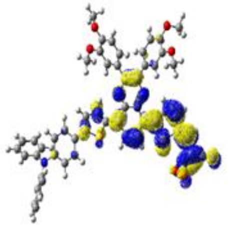
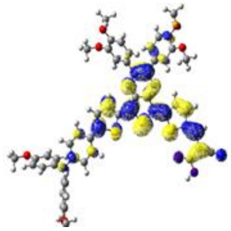
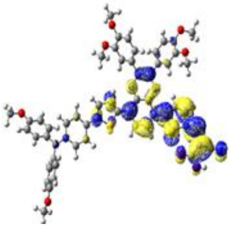


Fig. S3 Schematic division and dihedral angles of **MD** dyes.

dye	**MD4**	**MD5**	**MD6**	**MD7**
LUMO+2				
LUMO+1				
LUMO				

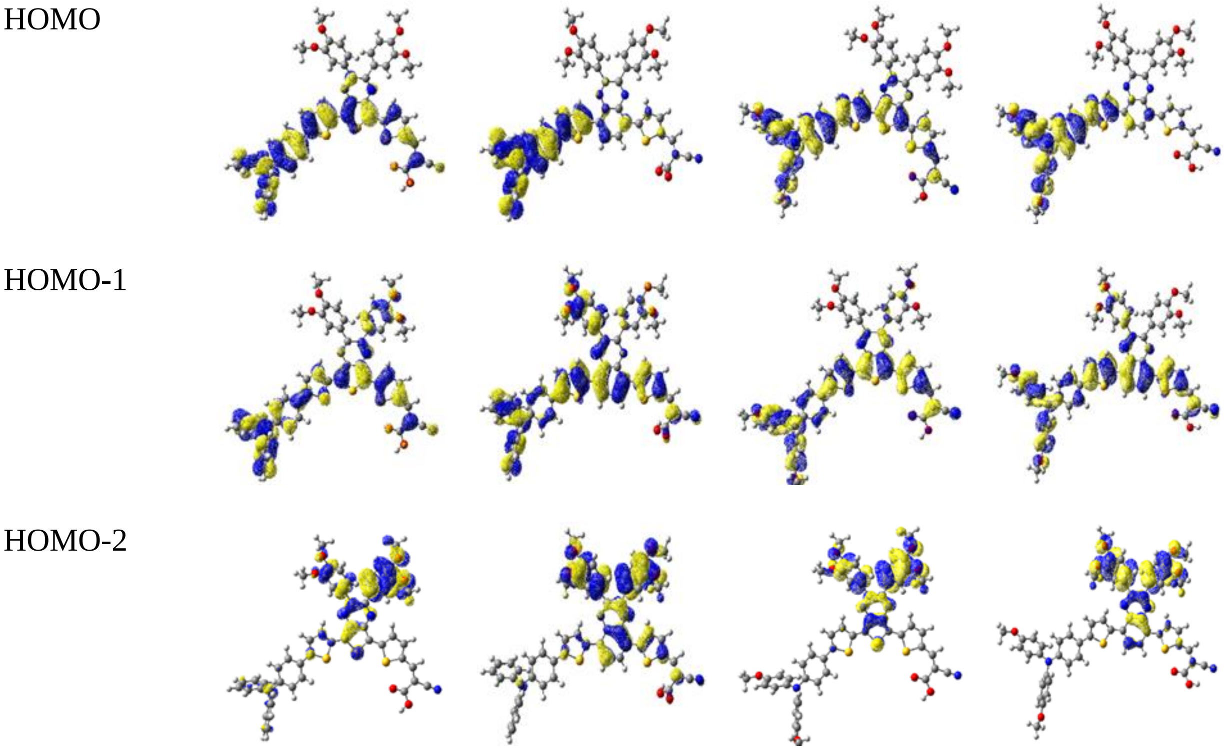


Fig. S4 Frontier orbitals of MD dyes.

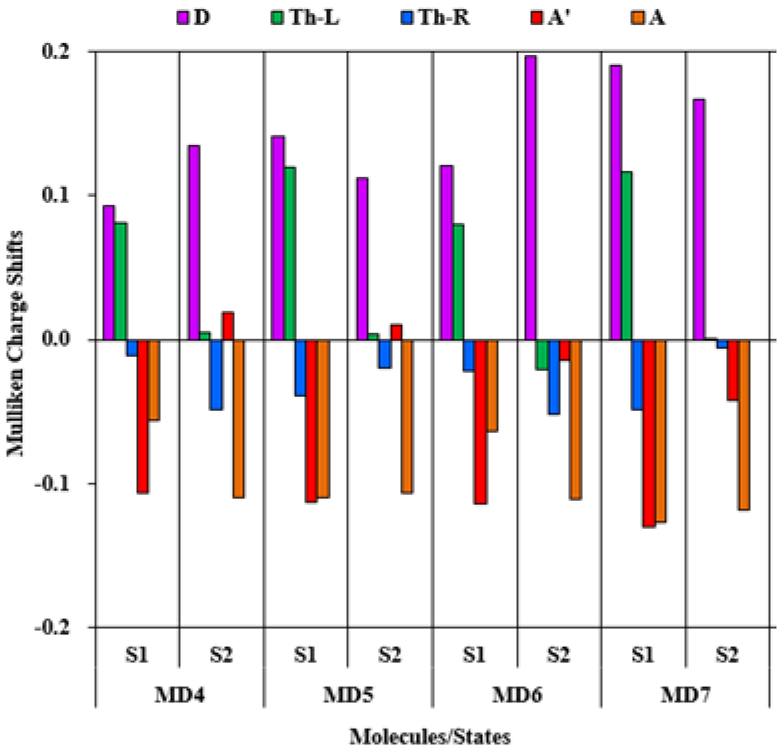


Fig. S5 Plot of the difference in the Mulliken charges between the ground and excited states.

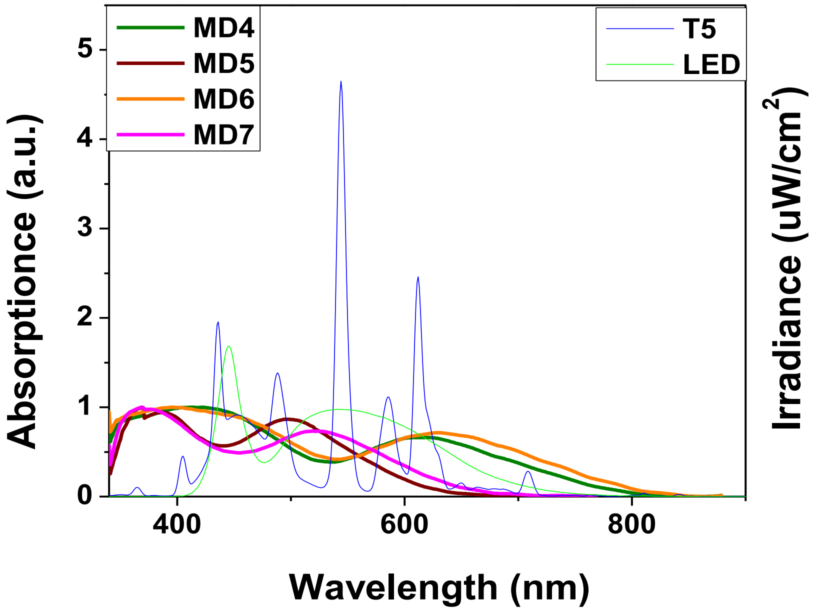


Fig. S6 The absorption spectra of **MD** dyes and the emission spectrum of T5 lamp.

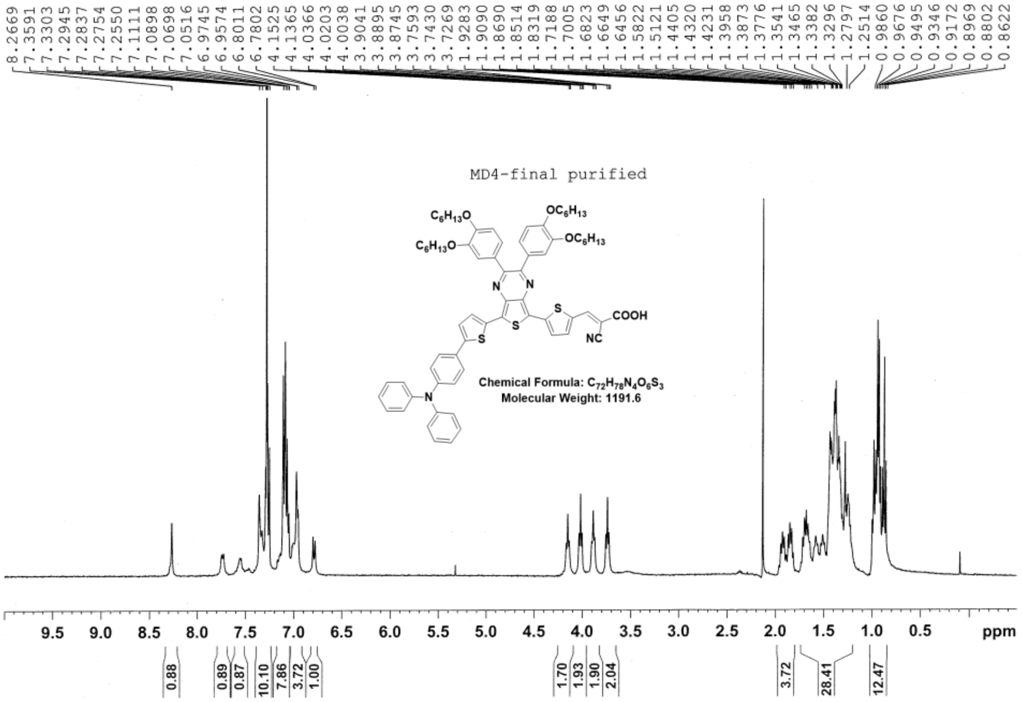


Fig. S7 ^{1}H NMR spectra of **MD4**.

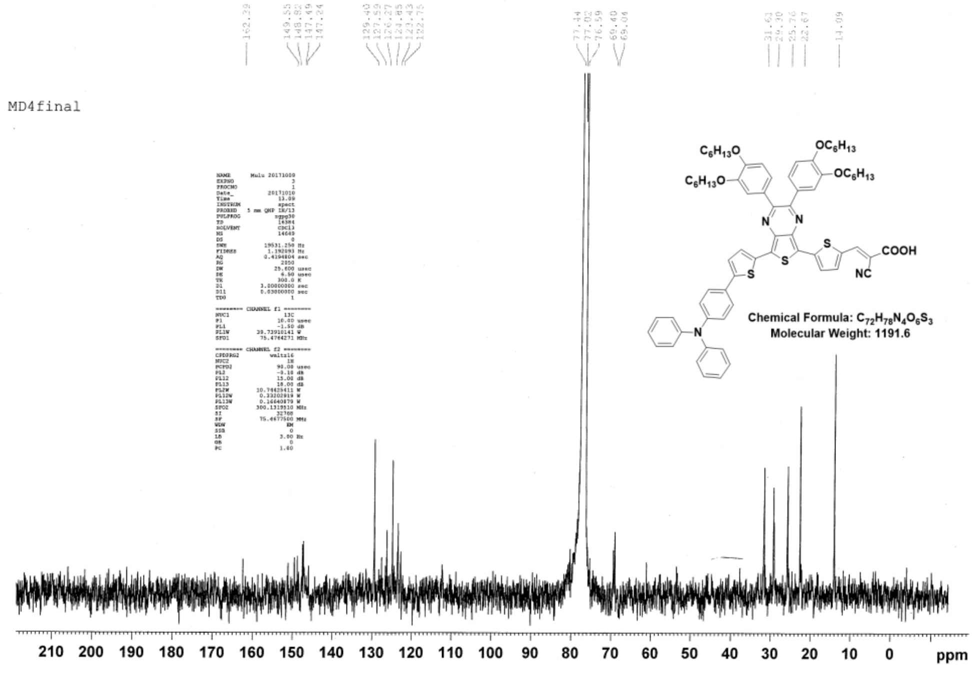


Fig. S8 ^{13}C NMR of **MD4**.

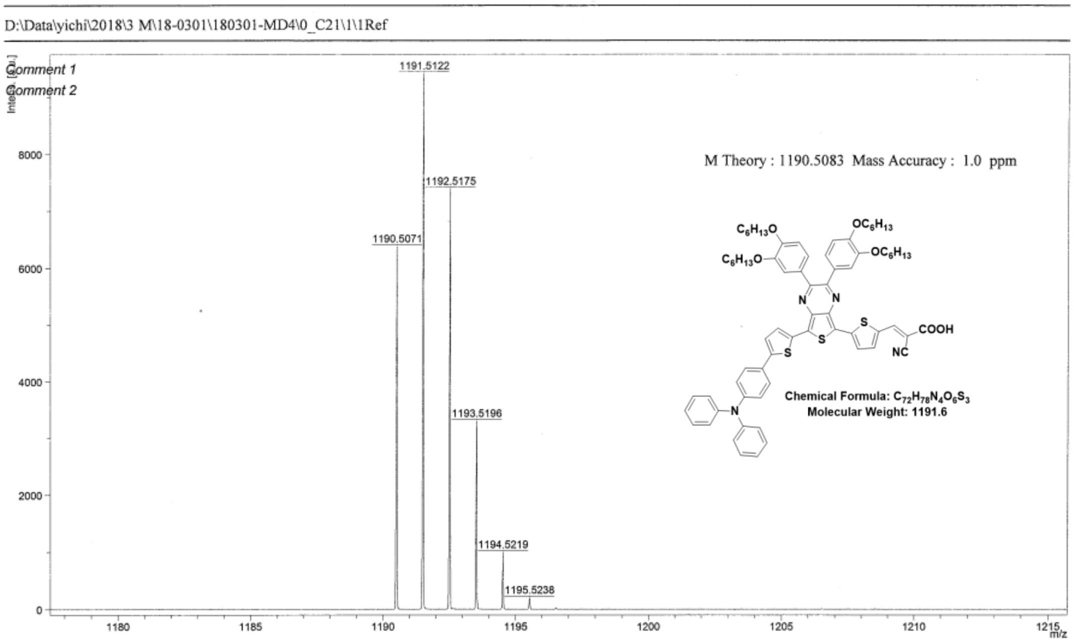
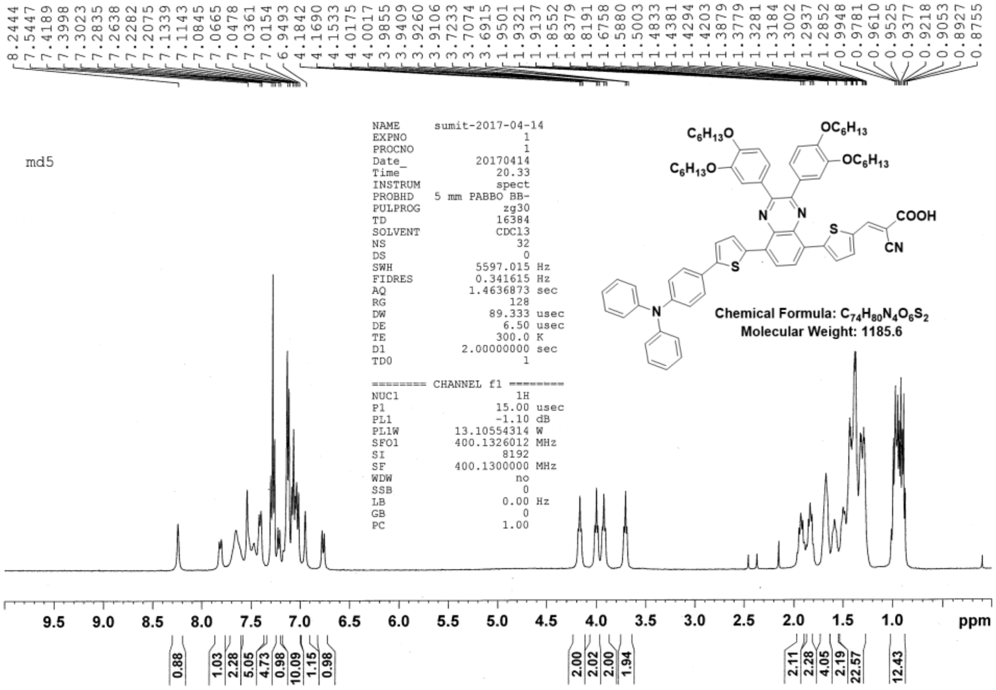


Fig S9. MS spectra of **MD4.**



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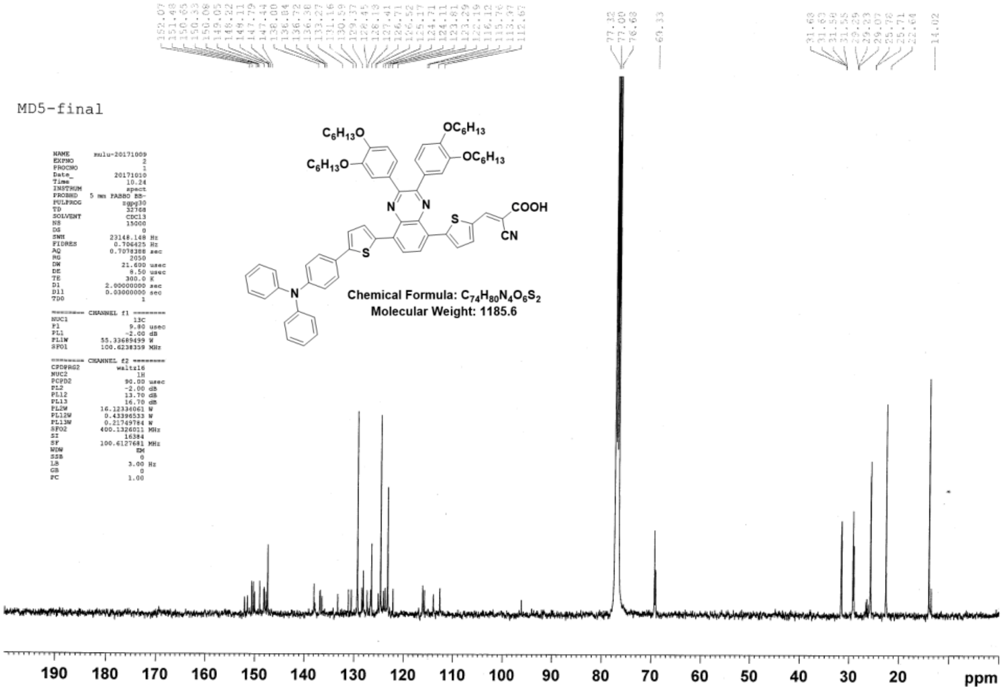
EXPNO                    1
PROCNO                   1
Date_             20170414
Time                 20.33
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                      32
DS                       0
SWH           5597.015 Hz
FIDRES        0.341615 Hz
AQ           1.4636873 sec
RG                     128
DW              89.333 usec
DE                6.50 usec
TE               300.0 K
D1          2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1               15.00 usec
PL1              -1.10 dB
PL1W       13.10554314 W
SFO1       400.1326012 MHz
SI                    8192
SF         400.1300000 MHz
WDW                     no
SSB                      0
LB                0.00 Hz
GB                       0
PC                    1.00
```

Fig. S10 ^{1}H NMR spectra of **MD5**.



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EXPNO                  2
PROCNO                 1
Date_           20171010
Time               10.24
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                 15000
DS                     0
SWH            23148.148 Hz
FIDRES          0.706425 Hz
AQ             0.7078388 sec
RG                  2050
DW                21.600 usec
DE                  8.50 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.80 usec
PL1                -2.00 dB
PL1W         55.33689499 W
SFO1         100.6238359 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -2.00 dB
PL12               13.70 dB
PL13               16.70 dB
PL2W         16.12334061 W
PL12W         0.43396533 W
PL13W         0.21749784 W
SFO2         400.1326011 MHz
SI                 16384
SF           100.6127681 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```

Fig. S11 ^{13}C NMR spectra of **MD5**.

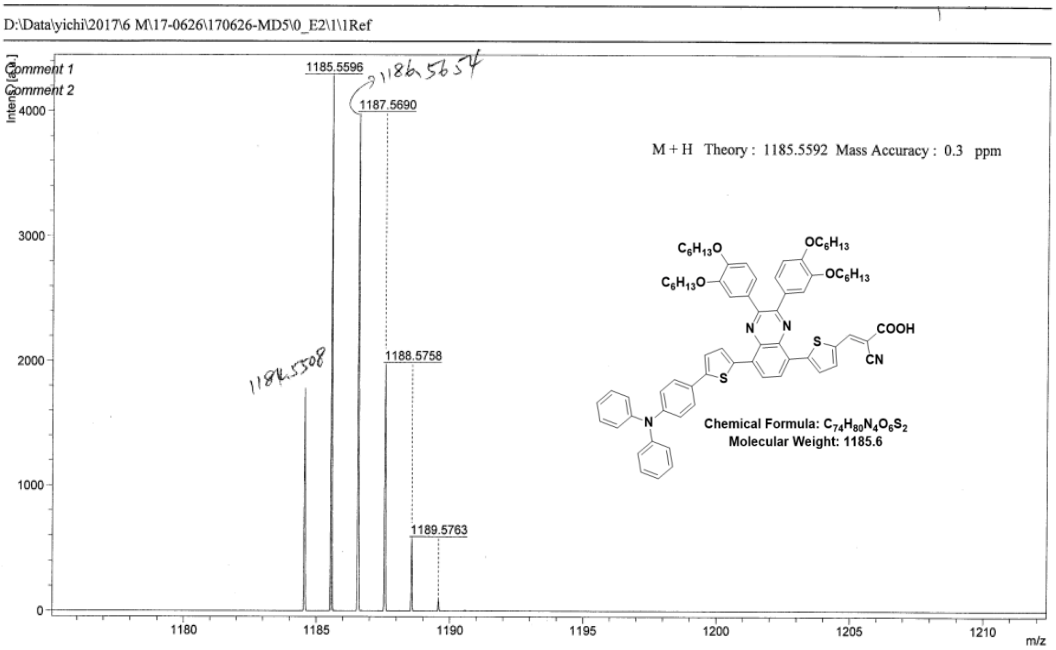


Fig. S12 MS spectra of **MD5**.

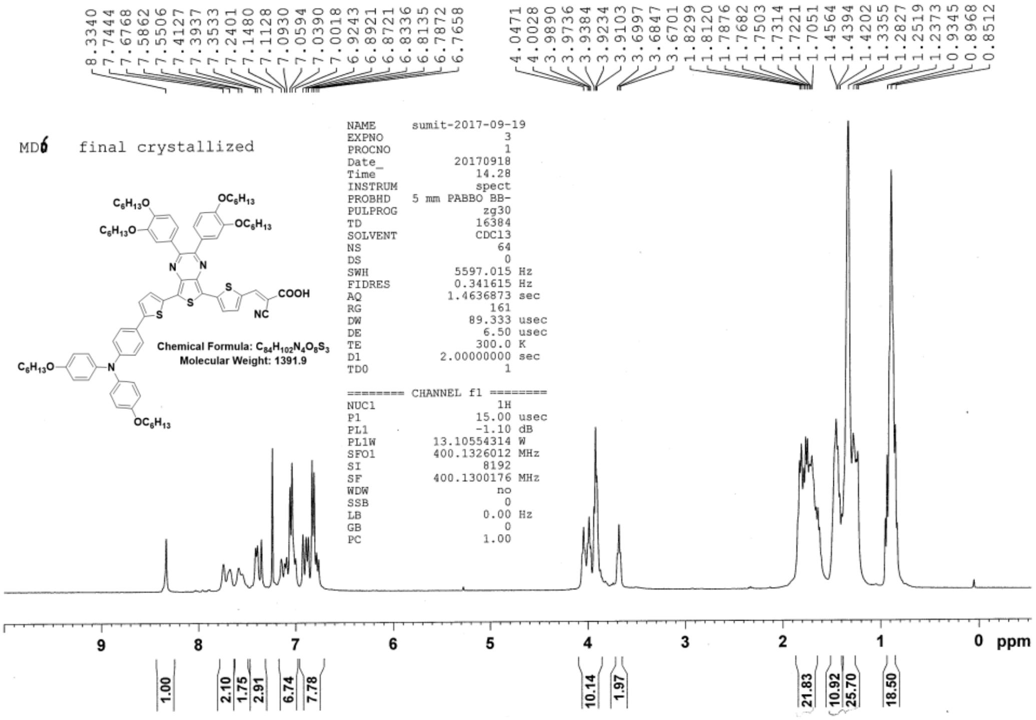


Fig. S13 ^{1}H spectra of **MD6**.

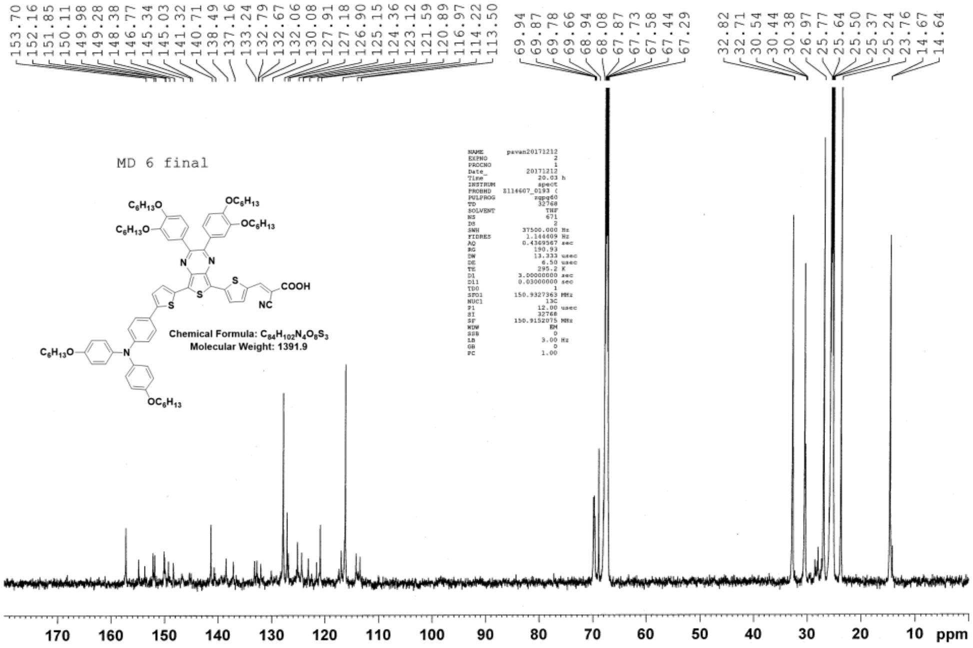
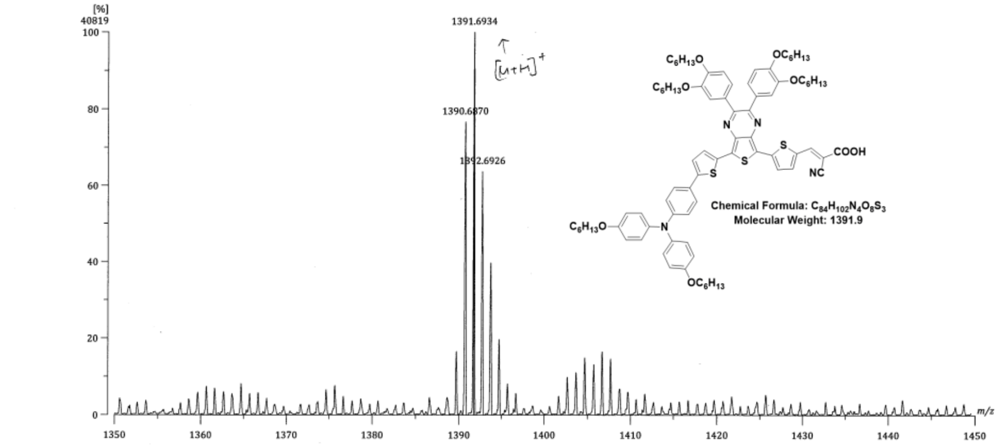


Fig. S14 ^{13}C spectra of **MD6**.

MD6 (HR-FAB)

[Mass Spectrum]
Data : 20180129_MD6-HR-001 Date : 29-Jan-2018 17:20
Sample : MD6
Note : NBA
Ion Mode : FAB+
RT : 0.00 min Scan# : 1
Elements : C 1000/0, H 1000/0, N 4/4, O 8/8, S 3/3
Mass Tolerance : 50mmu
Unsaturation (U.S.) : -0.5 - 1000.0



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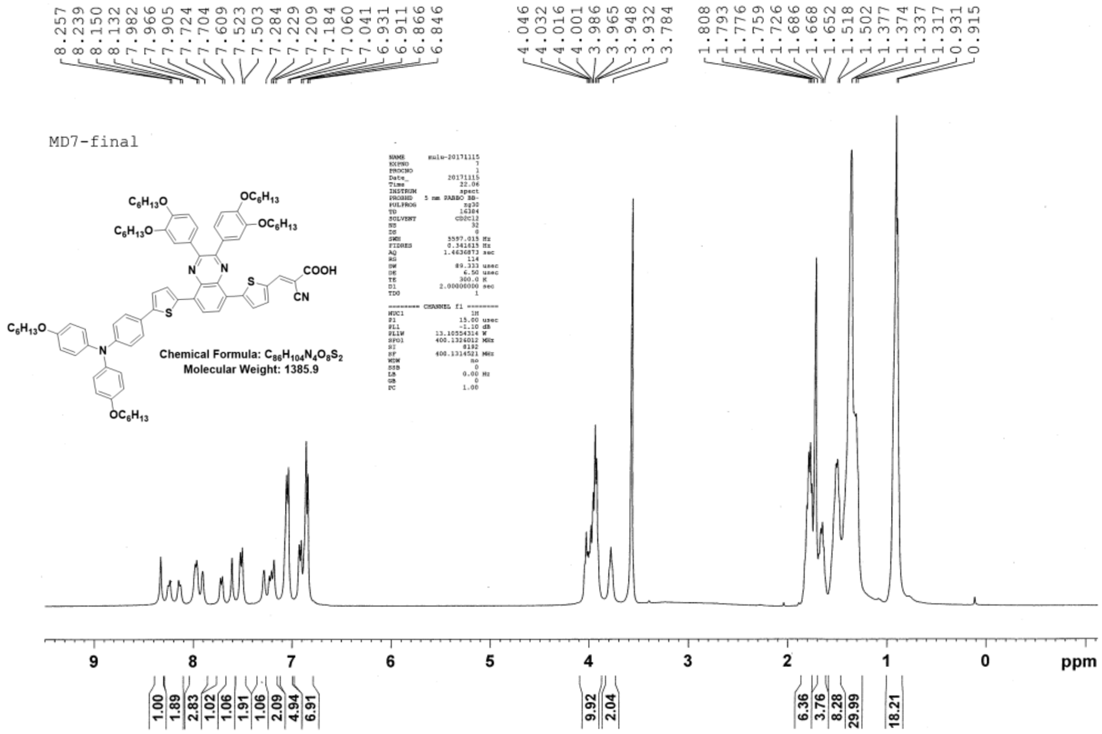
 Observed m/z  Int%     Err[ppm / mmu]   U.S.  Composition
1  1391.6934  100.00     -0.3 /  -0.4   38.5  C84 H103 N4 O8 S3  = 1391.6938
```

Fig. S15 MS spectra of **MD6**.



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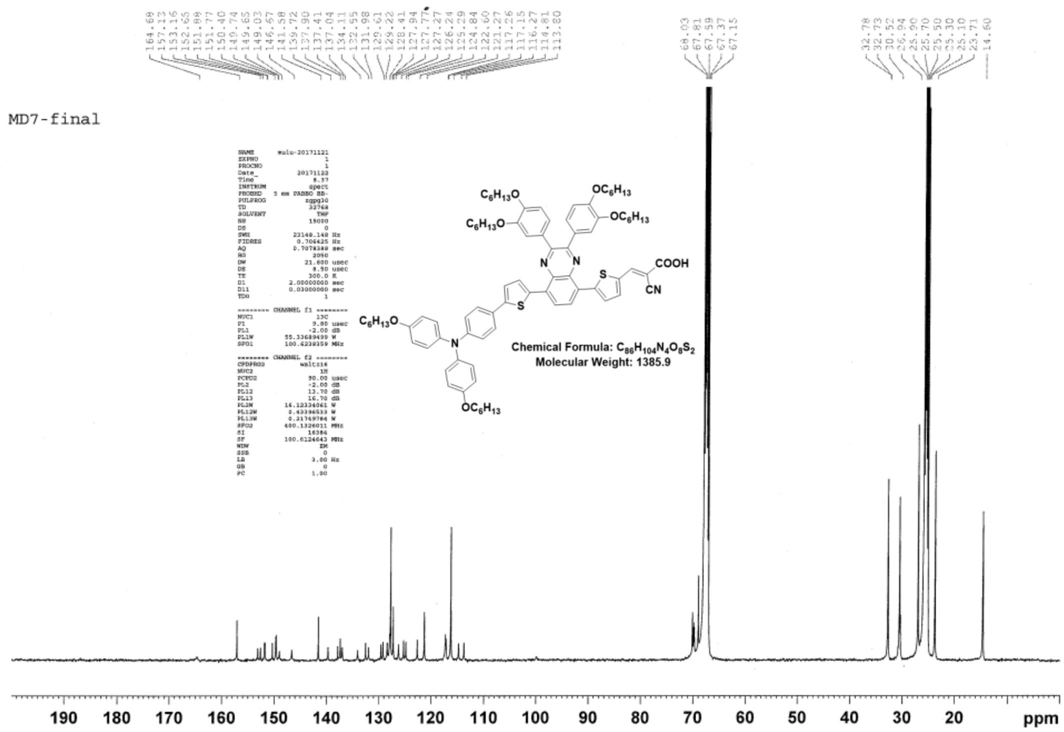
EXPNO               7
PROCNO              1
Date_        20171115
Time            22.06
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              16384
SOLVENT         CD2Cl2
NS                 32
DS                  0
SWH          5597.015 Hz
FIDRES       0.341615 Hz
AQ          1.4636873 sec
RG                114
DW             89.333 usec
DE               6.50 usec
TE              300.0 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              15.00 usec
PL1             -1.10 dB
PL1W      13.10554314 W
SFO1      400.1326012 MHz
SI               8192
SF        400.1314521 MHz
WDW                no
SSB                 0
LB               0.00 Hz
GB                  0
PC               1.00
```

Fig. S16 ^{1}H spectra of **MD7**.



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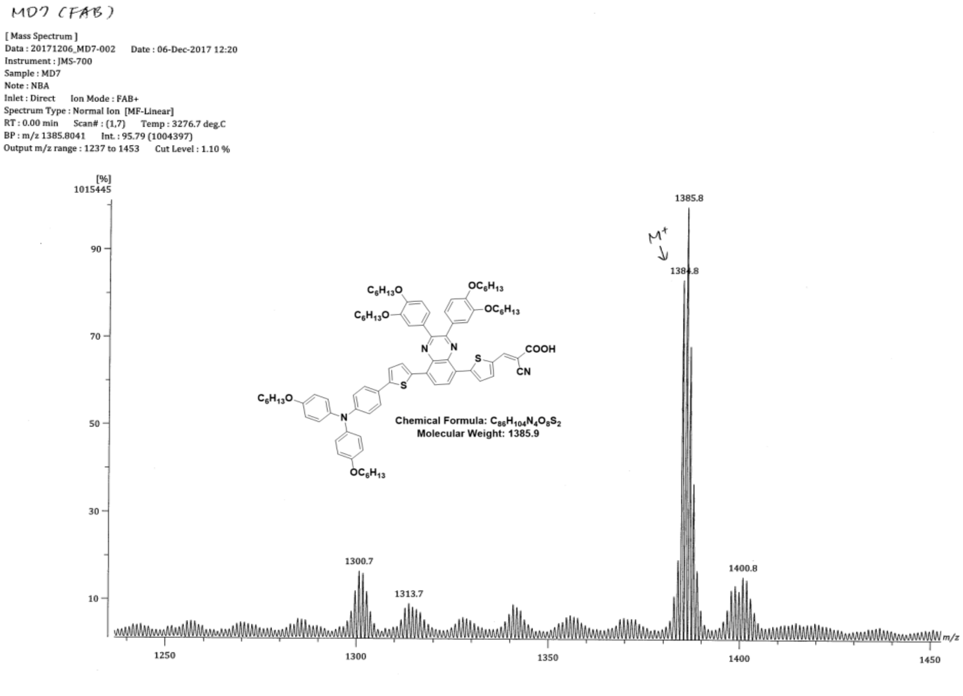
EXPNO                   1
PROCNO                  1
Date_            20171122
Time                 8.37
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  32768
SOLVENT               THF
NS                  15000
DS                      0
SWH            23148.148 Hz
FIDRES          0.706425 Hz
AQ             0.7078388 sec
RG                   2050
DW                 21.600 usec
DE                   6.50 usec
TE                  300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.80 usec
PL1                 -2.00 dB
PL1W          55.33689499 W
SFO1          100.6238359 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -2.00 dB
PL12                13.70 dB
PL13                16.70 dB
PL2W          16.12334061 W
PL12W          0.43396533 W
PL13W          0.21769784 W
SFO2          400.1326011 MHz
SI                  16384
SF            100.6124643 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.00
```

Fig. S17 ^{13}C spectra of **MD7**.



MD7 (FAB)

[Mass Spectrum]
Data : 20171206_MD7-002   Date : 06-Dec-2017 12:20
Instrument : JMS-700
Sample : MD7
Note : NBA
Inlet : Direct   Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.00 min   Scan# : (1,7)   Temp : 3276.7 deg.C
BP : m/z 1385.8041   Int. : 95.79 (1004397)
Output m/z range : 1237 to 1453   Cut Level : 1.10 %

Fig. S18 MS spectra of **MD7**.

References

[1] C.-T. Li, C.-P. Lee, M.-S. Fan, P.-Y. Chen, R. Vittal and K.-C. Ho, *Nano Energy*, 2014, ***9***, 1–14.

[2] B. O'Regan, L. Xiaoe and T. Ghaddar, *Energy Environ. Sci.*, 2012, ***5***, 7203−7215.