Supporting Information

Organic Dyes Incorporating Bis-Hexapropyltruxeneamino Moiety for Efficient Dye-Sensitized Solar Cells

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List of Contents

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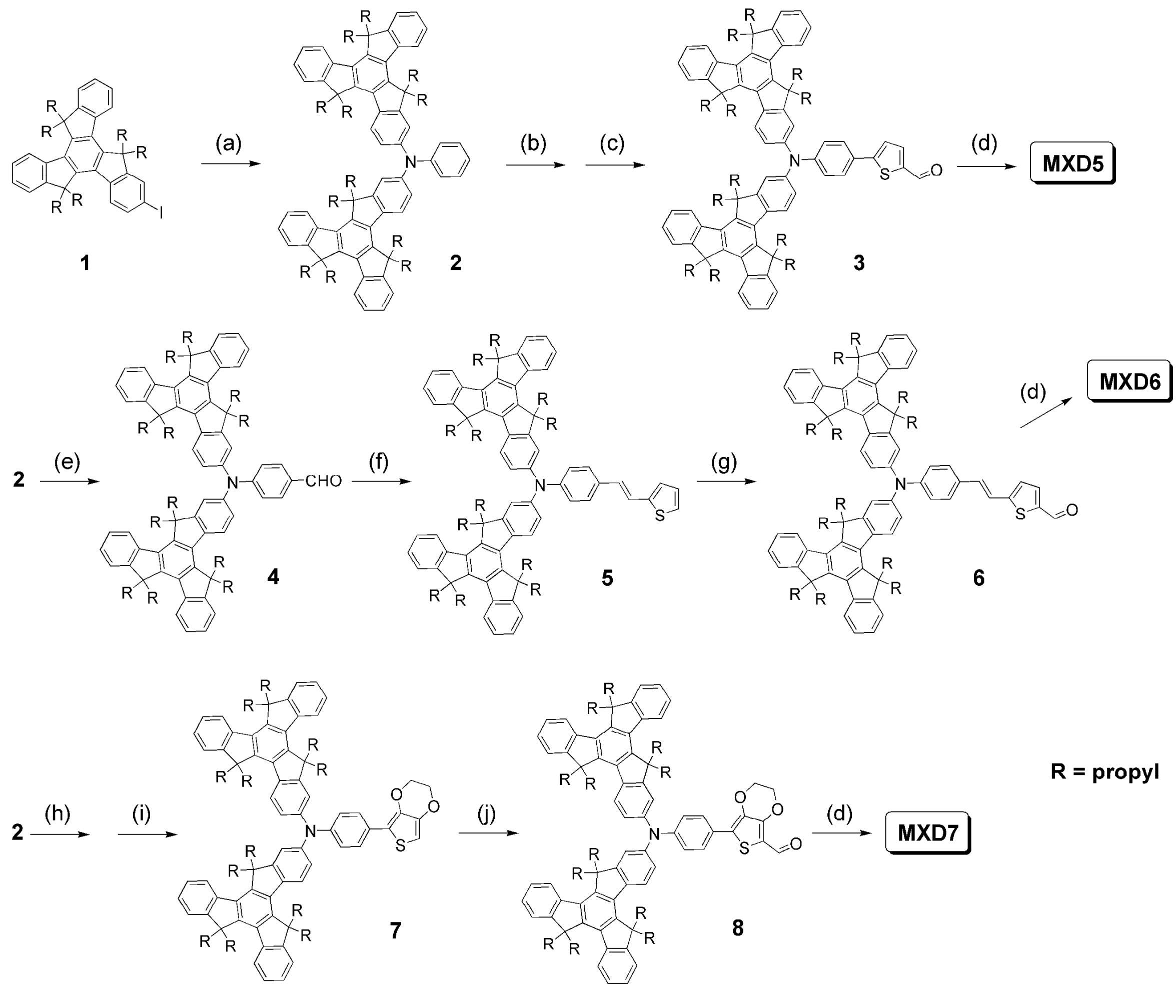
1. Synthesis and characterization.

1.1 General

The synthesis was carried out as outlined in Scheme **1**. Treatment of Iodide-substituted truxene **1** with powdered anhydrous potassium carbonate, copper bronze and 18-crown-6 afforded a key intermediate **2**. Aldehyde **3** was prepared from **2** via bromonation reaction with NBS and Suzuki reaction with 5-formylthiophen-2-ylboronic acid according to literature procedure. Aldehyde **4** was synthesized by Vilsmeier-Haack reaction of **2** with $POCl_3$ and DMF, and then cross-coupled with ethyl methyl(thiophen-2-ylmethyl)phosphinate under wittig-Horner reaction to give aldehyde **5**. Aldehyde **8** was prepared from **2** via iodonation reaction with NIS and stille reaction with 2-(tributylstannyl)-3,4-(ethelenedioxy)thiophene. The synthetic procedure for aldehyde **6, 9** were similar to that for aldehyde **4** except temperature shown in Scheme **2**. Subsequently, the target dye **MXD5-7** were obtained via Knoevenagel condensation reaction of the aldehyde **3**, **6, 9** with cyanoacetic acid in the presence of a catalytic amount of piperidine.



Scheme 1. Synthetic Routes to the **MXD5-7** Dyes (R = propyl) [a]

[a] (a) aniline, Cu powder, 18-Crown-6, K_2CO_3, 1,2-dichlorobenzene, reflux. (b) NIS, $CHCl_3$. (c) 5-formylthiophen-2-ylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, DME/H_2O, reflux. (d) $CNCH_2COOH$, CH_3CN,

piperidine, reflux. (e) DMF/$POCl_3$, 100 ℃. (f) ethyl methyl(thiophen-2-ylmethyl)phosphinate, Bu^tOK, THF. (g) DMF/$POCl_3$, 50 ℃. (h) NBS, $CHCl_3$. (i) 2-(Tributylstannyl)-3,4-(ethelenedioxy)thiophene, $Pd(PPh_3)_4$, toluene, reflux. (j) DMF/$POCl_3$, rt.

Synthesis of Triarylamine 2

A mixture of truxene iodide **1** (4.6 g, 6.39 mmol), aniline (0.238 g, 2.56 mmol), fresh Cu (0.63 g, 9.84 mmol) powder, K_2CO_3 (1.763 g, 12.8 mmol) powder, 18-crown-6 ether (0.124 g, 2.48 mmol) and 1,2-dichlorobenzene (50 mL) was refluxed for 18 h under nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure. Ethyl acetate was added before cooling down to room temperature. The organic layer was separated and washed 3 times with water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent, the resulting solid was purified by column chromatography on silica gel (petroleum : dichloromethane = 10 : 1 as eluent) to give a buff powder (2.9 g, 35.1%). Mp: 155-157 ℃. IR (KBr): 1396, 1457, 1559, 3464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.30-8.42 (m, 6H), 7.35-7.54 (m, 21H), 2.90-2.92 (m, 12H), 2.06-2.09 (m, 12H), 0.49-0.79 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 153.7, 153.6, 145.0, 144.8, 144.6, 144.3, 140.4, 140.3, 140.2, 138.5, 138.3, 129.2, 126.3, 126.0, 124.7, 124.6, 122.4, 122.3, 55.8, 55.7, 55.6, 39.5, 39.4, 39.3, 39.2, 29.8, 29.6, 17.6, 17.5, 17.4, 17.3, 14.7, 14.6 14.4. HRMS (ESI) calcd for $C_{96}H_{111}N$ ($M+H^+$): 1278.8707. Found: 1278.8696.

Synthesis of Carbaldehyde 3

Compound **2** (500 mg, 0.39 mmol) and NIS (90 mg, 0.39 mmol) were dissolved in chloroform (10 mL) and stirred at 0 ℃ for 2 h. The mixture was poured into water and extracted with dichloromethane. Then drying over anhydrous $MgSO_4$, the product was afforded after removing solvent as pink powder. After 5-formylthiophen-2-ylboronic acid (74 mg, 0.47 mmol), $Pd(PPh_3)_4$ (50 mg, 0.042 mmol), aqueous 1 M Na_2CO_3 (3 mL), and 10 mL DME was added, the mixture was refluxed overnight under nitrogen atmosphere. Ethyl acetate (10 mL) was added before cooling down to room temperature. The organic layer was separated and washed 3 times with water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent, the resulting solid was purified by column chromatography on silica gel (petroleum : ethyl acetate = 10 : 1 as eluent) to give an orange yellow powder **3** (230 mg, 42.3%). Mp: 70-72 °C. IR (KBr):1139, 1396, 1456, 1559, 3464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.28-8.42 (m, 6H), 7.22-7.56 (m, 23H), 2.89-2.92 (m, 12H), 1.92-2.19 (m, 12H), 0.5-0.78 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.9, 182.7, 155.5, 154.8, 154.4, 153.8, 153.6, 149.4, 145.3, 144.8, 144.6, 144.5, 142.5, 141.4, 140.3, 138.4, 138.3, 138.0, 137.9, 137.8, 137.5, 136.3, 129.5, 129.3, 128.9, 127.3, 126.5, 126.4, 126.1, 125.6, 124.7, 124.6, 122.9, 122.6, 122.4, 118.7, 55.8, 55.7, 55.6, 39.5, 39.4, 39.3, 39.1, 29.8, 29.6, 17.6, 17.5, 17.4, 17.3, 14.7, 14.6 14.4. HRMS (ESI) calcd for $C_{101}H_{113}NOS$ ($M+H^+$): 1388.8616. Found: 1388.8631.

Synthesis of MXD5

To a solution of compound **3** (170 mg, 0.12 mmol) and cyanoacetic acid (14 mg, 0.16 mmol) was added acetonitrile (10 mL), dichlormethane (5 mL) and piperidine (50 μL). The solution was refluxed for 24 h. After cooling the solution, the solvent was removed in vacuo. Dichloromethane was added. The organic layer was separated and washed 3 times with water, dried over anhydrous $MgSO_4$, and filtered. The pure product was obtained by silica gel chromatography (dichloromethane : methanol = 10 : 1 as eluent) to give a salmon pink powder **MXD5** (140 mg, 78.7%). Mp: 133-135 □. IR (KBr):1396, 1456, 1559, 2264, 2957, 3364 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.32-8.38 (m, 6H), 7.16-7.68 (m, 23H), 2.90-2.95 (m, 12H), 1.86-2.16 (m, 12H), 0.37-0.78 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 155.4, 153.7, 153.6, 145.3, 144.8, 144.5, 144.4, 140.3, 140.2, 138.3, 138.2, 137.9, 136.2, 126.4, 126.1, 125.5, 124.7, 122.9, 122.5, 122.3, 118.6, 60.5, 55.8, 55.7, 55.6, 39.4, 39.3, 39.2, 29.8, 17.5,17.3, 14.7, 14.6, 14.5. HRMS (ESI) calcd for $C_{104}H_{114}N_2O_2S$ ($M+H^+$): 1455.8674. Found: 1455.8682.

Synthesis of Carbaldehyde 4

To a solution of compound **2** (500 mg, 0.39 mmol) in anhydrous DMF (10 mL, 126 mmol) at 0 □ under nitrogen atmosphere was added $POCl_3$ (1 mL, 6.70 mmol) dropwise and stirred for 1 h. Subsequently, the mixture was heated at 100 □ for 4 h. The mixture was cooled and poured into an ice-water with vigorous stirring. After neutralization with NaOH, extraction with ethyl acetate, the organic fractions were combined and dried over $MgSO_4$. The resulting solid was purified by column chromatography on silica gel (petroleum: ethyl acetate = 10 : 1 as eluent) to give a bright yellow powder **4** (450 mg, 88.1%). Mp: 133-135 □. IR (KBr): 1396, 1456, 1559, 1637, 3464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.33-8.38 (m, 6H), 7.28-7.81 (m, 2H), 7.21-7.51 (m, 18H), 2.90-2.94 (m, 12H), 2.01-2.07 (m, 12H), 0.47-0.79 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 155.7, 153.8, 153.6, 153.5, 145.0, 144.8, 144.6, 140.3, 140.2, 138.5, 138.4, 137.8, 137.5, 131.5, 126.6, 126.2, 125.8, 124.8, 124.7, 124.0, 122.5, 122.4, 120.0, 55.9, 55.8, 55.7, 39.5, 39.3, 39.1, 38.9, 30.3, 29.8, 29.6, 23.1, 22.9, 22.8, 20.3, 19.3, 17.6, 17.4, 14.8, 14.7, 14.6. HRMS (ESI) calcd for $C_{97}H_{111}NO$ ($M+H^+$): 1306.8739. Found: 1306.8769.

Synthesis of Compound 5.

To a suspension of ethyl methyl(thiophen-2-ylmethyl)phosphinate (98 mg, 0.42 mmol) in 20 mL dry THF at 0 □ under nitrogen atmosphere, Bu^tOK (47 mg, 0.42 mmol) was added and the mixture turned red. The mixture was stirred at this temperature for 1 h before compound 4 (180mg, 0.14mmol) dissolved in 10 ml dry THF was added dropwise. The mixture was stirred at 0 □ for 1 h and moved into room temperature for another 12 h. Saturated NH_4Cl was added and the resulting mixture was extracted with Ethyl acetate. The combined extracts were washed with water and dried over $MgSO_4$. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography on silica gel (petroleum : dichloromethane= 10 : 1 as eluent) to give a yellow powder **5** (120 mg, 64.8%). Mp: 91-93 □. IR(KBr):1103, 1396, 1487, 3464 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.22-8.42 (m, 6H), 7.16-7.52 (m, 22H), 6.89-7.14 (m, 3H), 2.86-3.03 (m, 12H), 1.93-2.19 (m, 12H), 0.52-0.83 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 153.8, 153.7, 147.6, 146.0, 145.9, 144.9, 144.4, 144.3, 143.4, 140.4, 140.3, 138.3, 138.2, 138.1, 135.6, 135.4, 131.1, 128.1, 127.8, 127.7, 127.2, 126.4, 126.1, 125.6, 125.4, 124.7, 123.9, 123.6, 122.4, 120.2, 118.1, 55.8, 55.7, 55.6, 39.5, 39.4, 39.3, 29.8, 29.6, 17.6, 17.4, 14.7, 14.6. HRMS (ESI) calcd for $C_{102}H_{115}NS$ ($M+H^+$): 1386.8823. Found: 1386.8808.

Synthesis of Carbaldehyde 6

The product was synthesized according to the procedure for synthesis of **4**, giving an orange powder **6** of the product in 79.6% yield. Mp: 95-96 □. IR (KBr): 1396, 1487, 1637, 3464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.25-8.42 (m, 6H), 7.69 (d, J = 13.9 Hz, 1H), 7.13-7.53 (m, 24H), 2.83-3.01 (m, 12H), 1.93-2.18 (m, 12H), 0.52-0.79 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.5, 155.4, 153.8, 153.7, 153.3, 145.5, 144.8, 144.6, 144.4, 140.4, 140.3, 138.3, 138.0, 137.5, 136.1, 132.8, 129.5, 128.0, 126.4, 126.1, 126.0, 125.5, 124.7, 124.6, 122.8, 122.4, 118.7, 118.5, 55.8, 55.7, 55.6, 39.4, 39.3, 29.8, 24.8, 22.8, 17.6, 17.4, 14.7, 14.6, 14.2. HRMS (ESI) calcd for $C_{103}H_{115}NOS$ ($M+H^+$):1414.8772. Found: 1414.8787.

Synthesis of MXD 6

The product was synthesized according to the procedure for synthesis of **MXD5**, giving a fuchsia powder **MXD6** of the product in 76.7% yield. Mp: 111-113 ℃. IR (KBr): 1487, 1637, 2263, 3374 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.30-8.74 (m, 8H), 7.16-7.58 (m, 23H), 2.93-2.99 (m, 12H), 1.95-2.21 (m, 12H), 0.51-0.79 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 168.1, 153.8, 153.7, 144.9, 140.4, 140.3, 138.4, 128.4, 124.7, 122.4, 118.7, 116.0, 112.6, 95.2, 55.8, 55.7, 39.4, 39.3, 31.7, 29.8, 29.6, 29.2, 29.0, 24.8, 22.9, 22.8, 22.7, 17.6, 17.4, 14.8, 14.7, 14.6, 14.2. HRMS (ESI) calcd for $C_{106}H_{116}N_2O_2S$ ($M+H^+$):1481.8813. Found: 1481.8844.

Synthesis of Compound 7.

Compound **2** (1.2 g, 0.94 mmol) and NBS (168 mg, 0.94 mmol) were dissolved in chloroform (12 mL) and stirred at 0 ℃ for 4 h. The mixture was poured into water and extracted with dichloromethane. Then drying over anhydrous $MgSO_4$, the product was afforded after removing solvent as buff powder. After 2-(tributylstannyl)-3,4-(ethelenedioxy)thiophene (700 mg, 0.62 mmol), $Pd(PPh_3)_4$ (110 mg, 0.092 mmol), and 50mL toluene was added, the mixture was refluxed for 7 h under nitrogen atmosphere. After cooling the solution, the solvent was removed in vacuo. Dichloromethane was added. The organic layer was separated and washed 3 times with water, dried over anhydrous $MgSO_4$, and filtered. The pure product was obtained by silica gel chromatography. (petroleum : dichloromethane = 10 : 1 as eluent) to give a yellow powder **7** (526 mg, 39.6%). Mp: 108-109 ℃. IR (KBr):1103, 1637, 3420 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.19-8.39 (m, 6H), 7.68 (d, J = 8.6 Hz, 2H), 7.14-7.49 (m, 18H), 6.28 (s, 1H), 4.29 (d, J = 8.7 Hz, 4H), 2.83-2.89 (m, 12H), 1.89-2.12 (m, 12H), 0.48-0.73 (m, 60H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 153.7, 146.5, 145.9, 144.8, 144.3, 144.2, 142.3, 140.4, 140.3, 138.2, 138.1, 137.6, 135.3, 128.6, 127.5, 126.9, 126.6, 126.3, 126.0, 125.4, 124.7, 123.9, 122.3, 122.1, 117.8, 117.6, 64.8, 64.5, 55.7, 55.6, 39.4, 39.3, 39.0, 29.7, 29.5, 29.4, 17.5, 17.3, 14.7, 14.6, 14.5. HRMS (ESI) calcd for $C_{102}H_{115}NO_2S$ ($M+H^+$):1418.8722. Found: 1418.8730.

Synthesis of Carbaldehyde 8.

The product was synthesized according to the procedure for synthesis of **4,** giving an orange powder **8** of the product in 76.6% yield. Mp: 122-124 ℃. IR (KBr): 1144, 1637, 3420 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.30-8.36 (m, 6H), 7.76 (d, *J* = 8.7Hz, 2H), 7.14-7.51 (m, 18H), 4.40 (d, *J* = 8.7 Hz, 4H), 2.89 (s, 12H), 1.86-2.18 (m, 12H), 0.47-0.73 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.4, 155.4, 155.3, 153.7, 153.6, 149.2, 148.6, 145.4, 144.8, 144.6, 144.4, 140.3, 140.2, 138.4, 138.3, 138.0, 137.0, 136.1, 129.6, 127.9, 126.4, 126.1, 125.5, 125.1, 124.7, 124.6, 122.8, 122.4, 122.3, 118.6, 114.8, 65.2, 64.6, 55.8, 55.7, 55.6, 39.4, 39.3, 39.2, 29.7, 29.5, 17.5, 17.3, 14.6, 14.5, 14.4. HRMS (ESI) calcd for $C_{103}H_{115}NO_3S$ ($M+H^+$):1446.8670. Found: 1446.8641.

Synthesis of MXD7.

The product was synthesized according to the procedure for synthesis of **MXD5**, giving a red powder **MXD7** of the product in 71.7% yield. Mp: 140-142 ℃. IR (KBr): 1144, 2264, 3364 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23-8.52 (m, 7H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.18-7.50 (m, 18H), 4.42-4.45 (m, 4H), 2.89-2.93 (m, 12H), 1.91-2.16 (m, 12H), 0.48-0.78 (m, 60H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 153.7, 153.6, 145.3, 144.8, 144.6, 144.4, 140.3, 140.2, 138.3, 138.2, 137.9, 137.2, 136.3, 128.2, 126.4, 126.0, 125.5, 124.7, 123.0, 122.3, 118.7, 64.7, 60.4, 55.8, 55.7, 55.6, 39.4, 39.3, 39.2, 30.3, 29.7, 17.5, 17.3, 14.6, 14.5. HRMS (ESI) calcd for $C_{106}H_{116}N_2O_4S$ ($M+H^+$):1513.8729. Found: 1513.8797.

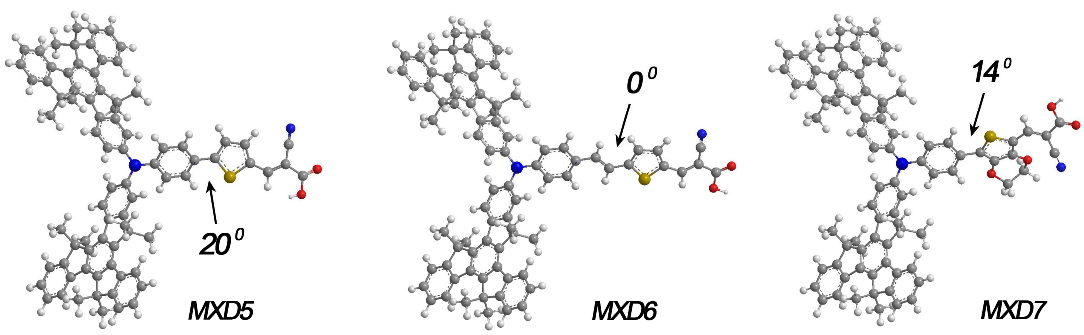


Figure S1. Optimized geometrical configuration of **MXD5–7.**

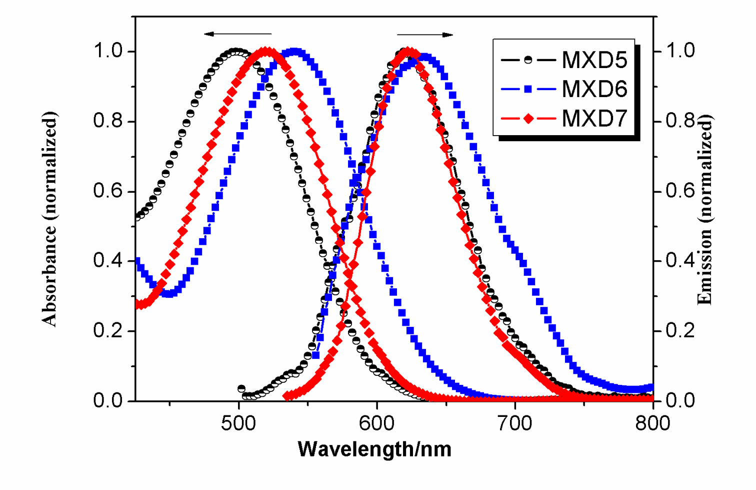


Figure S2. Absorption and emission spectra of dyes **MXD5-7** in dichloromethane

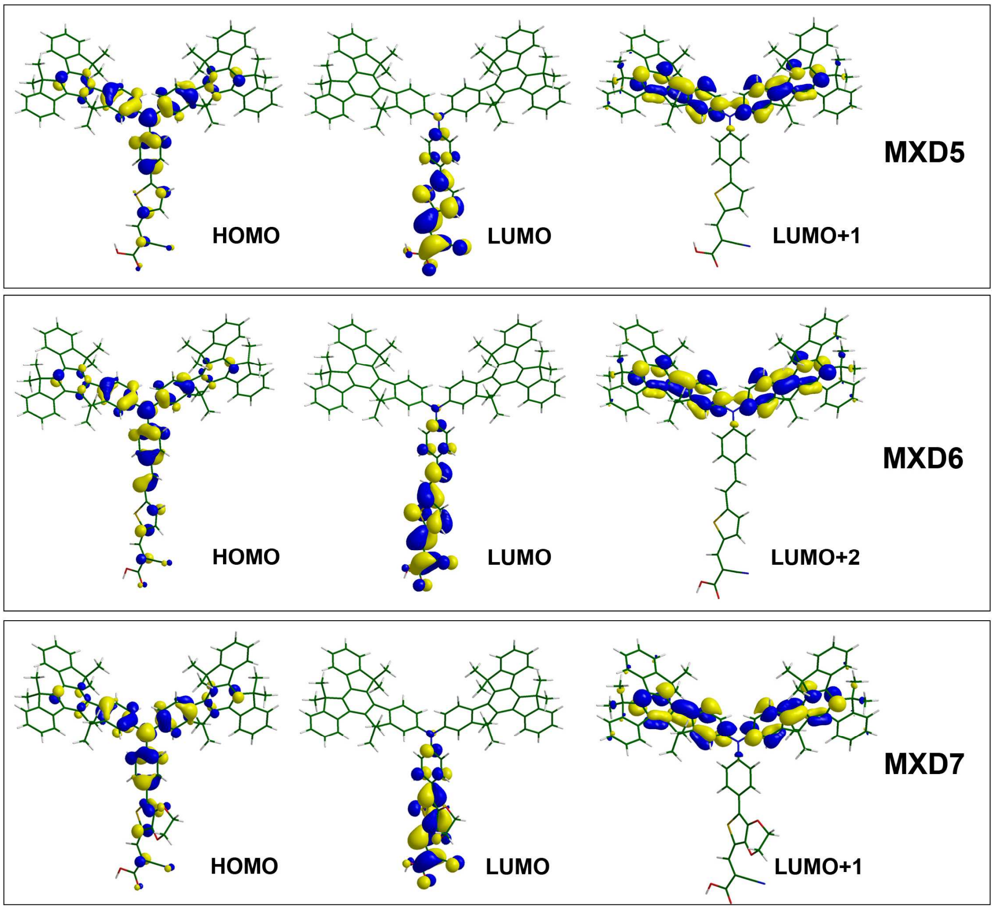


Figure S3. Frontier molecular orbitals of the **MXD5-7** dyes calculated at B3LYP/6-31+g(d) level.

Table S1. Calculated TDDFT Excitation Energies (eV, nm), Oscillator Strengths (*f*), and Molecular Orbital Transition assignment.[a]

State	E(ev, nm)	*f*	Transition assignment	
1	2.16 (572)	0.64	H→ L(89%)	MXD5
5	3.03 (408)	0.54	H-4→ L(84%)	
6	3.29 (376)	0.80	H→ L+1(89%)	
7	3.41 (363)	0.35	H-5→ L(37%); H→ L+2(56%)	
1	2.10 (589)	0.97	H→ L(87%)	MXD6
4	2.88 (429)	0.92	H-3→ L(72%)	
6	3.21 (386)	0.19	H-3→ L(2%); H→ L+1(60%); H→ L+2(6%)	
7	3.23 (383)	0.71	H-5→ L(3%); H→ L+2(84%)	
1	2.28 (544)	0.74	H→ L(89%)	MXD7
4	3.12 (396)	0.13	H-3→ L(72%); H-2→ L(23%)	
5	3.13 (395)	0.57	H-2→ L(56%); H→ L+2(4%)	
6	3.23 (383)	0.85	H→ L+1(89%)	

[a]Incorporating the optimized model at the B3LYP/6-31G(d) level in vacuo, the lowest 10 singlet-singlet electronic transitions are calculated. Transitions with *f*< 0.1 are not shown.

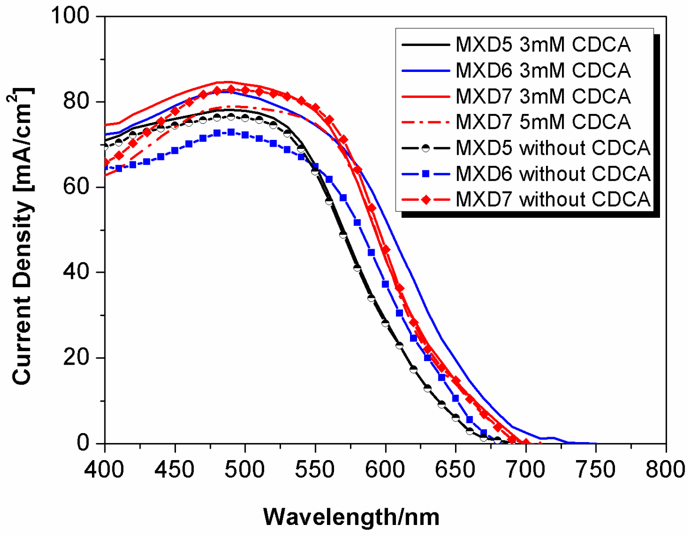


Figure S4. IPCE spectra for DSSCs based on **MXD5-7** with and without the addition of CDCA

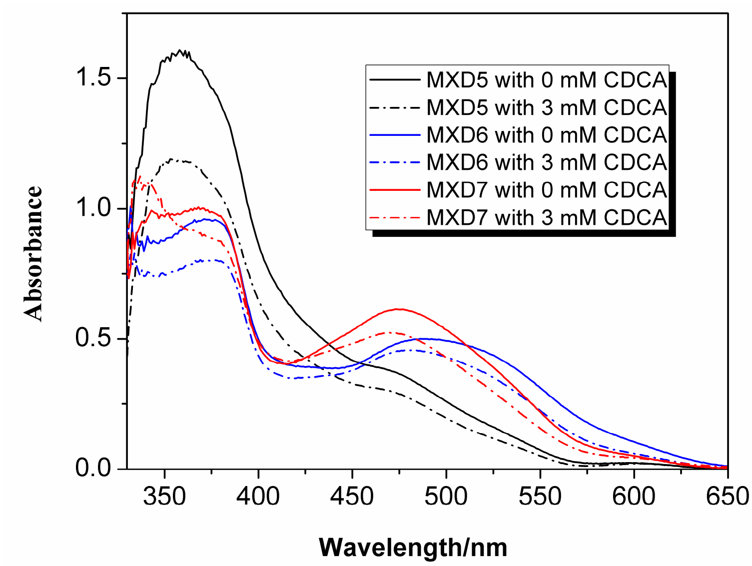


Figure S5. Absorption spectra for TiO_2 films (3 μm) exposed to dye solutions containing 0 and 3 mM CDCA. There are no significant changes between the maximum absorption wavelengths of **MXD5-7** on the TiO_2 film with and without CDCA addition, indicating that the possible π-stacked aggregation is not obvious.

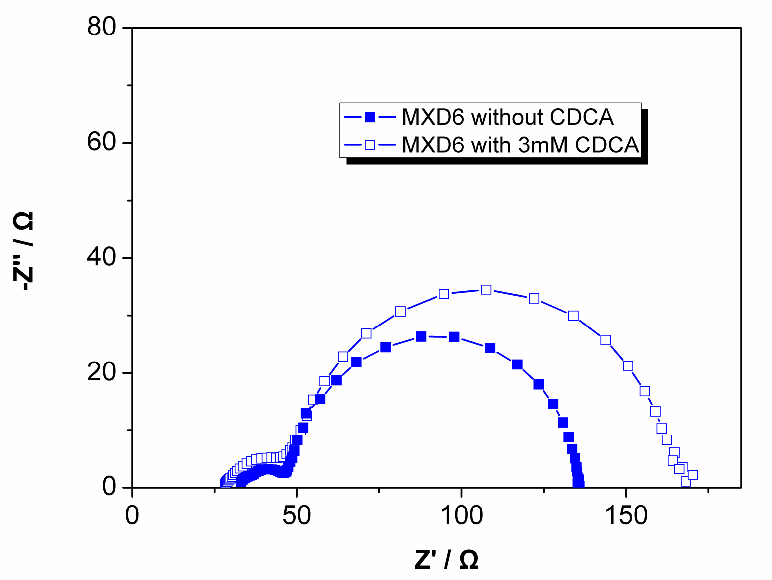


Figure S6. EIS for DSSCs based on the **MXD6** dye with and without the addition of CDCA measured in the dark under -0.7V bias displayed in the form of Nyquist plots.

References

[S1] Xiao-Yu Cao, Wei Zhang, Hong Zi, and Jian Pei, *Org. Lett.*, 2004, **26**, 4845.