

Electronic Supplementary Information for

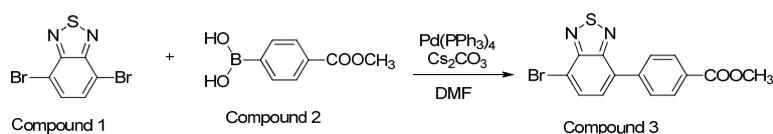
**A Large, Ultra Black, Efficient and Cost-effective
Dye-sensitized Solar Module Approaching 12% Overall
Efficiency under 1000 Lux Indoor Light**

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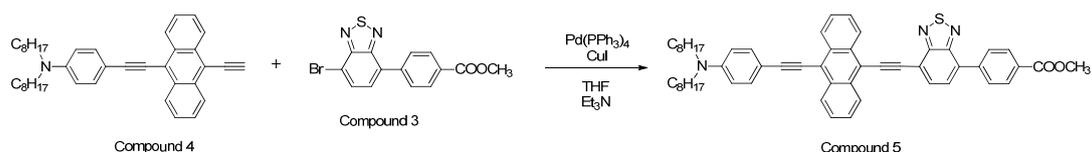
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Dye Synthesis and Characterization



Compound 3

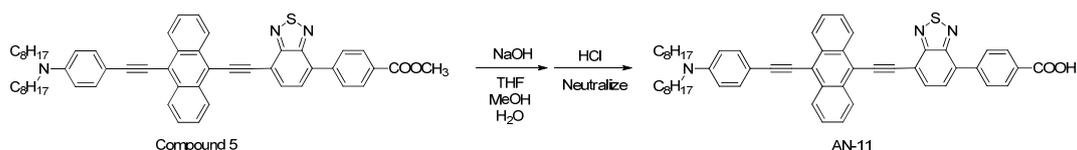
312 mg of compound 1 (M.W. = 293.96 g/mol, 1.061 mmol, 1.05 equiv.) was mixed with 180 mg of compound 2 (M.W. = 179.96 g/mol, 1.000 mmol, 1.00 equiv.) and 656mg of caesium carbonate (M.W. = 325.82 g/mol, 2.013 mmol, 2.00 equiv.) in 20 ml of toluene/DMF co-solvent (v/v, 1/1). The mixture was then degassed by nitrogen bubble and sonic, followed by adding 118 mg of Pd(PPh₃)₄ (M.W. = 1155.56, 0.102 mmol, 0.01 equiv.). The reaction was stirred at 100°C for 17 hours. The completion of the reaction was monitored by TLC. After cooled down, the toluene was removed with rotary evaporation, then poured the mixture in to water and collected the precipitation by filtration. The collected solid was re-dissolved in ethyl acetate for washing with NH₄Cl_(aq). After drying over Na₂SO₄, the solvent was removed with rotary evaporation. The residue was purified on a column chromatograph (silica gel, eluent THF/n-hexanes = 1/5) to give compound 3 (light yellow solid, 205mg, yield: 58%). ¹H-NMR (CDCl₃ at 7.26 ppm, 300 MHz): δ_H(ppm): 8.19 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 7.7 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 3.97 (s, 3H).



Compound 5

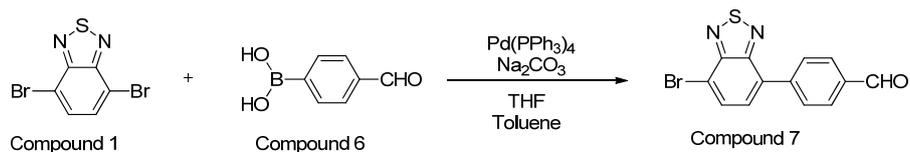
321 mg of compound 4 (M.W. = 541.81 g/mol, 0.592 mmol, 1.00 equiv.)^{S1} was mixed with 186 mg of compound 3 (M.W. = 349.20 g/mol, 0.532 mmol, 0.9 equiv.) in 35 ml of THF and 5 ml of Et₃N. After 3 cycles of freeze–pump–thaw, 10 mol % of Pd(PPh₃)₄ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50 °C for 40 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH₂Cl₂ for NH₄Cl_(aq) washes. After dried over Na₂SO₄, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/n-hexanes = 1/3 as eluent, followed by crystallization from CH₂Cl₂/MeOH to give compound 5 (dark red solid, 205mg, yield:

70%). ^1H NMR (CDCl_3 , 300 MHz), δ_{H} (ppm): 8.95 (d, $J = 8.7$ Hz, 2H); 8.75 (d, $J = 8.4$ Hz, 2H); 8.24 (d, $J = 8.5$ Hz, 2H); 8.11 (d, $J = 8.9$ Hz, 2H); 7.86 (d, $J = 7.4$ Hz, 1H); 7.78-7.55 (m, 7H); 6.68 (d, $J = 9.2$ Hz, 2H); 3.99 (s, 3H); 3.47-3.19 (m, 4H); 1.59 (s, 4H), 1.40-1.22 (m, overlapped, 20H); 1.02-0.78 (m, 6H).



AN-11

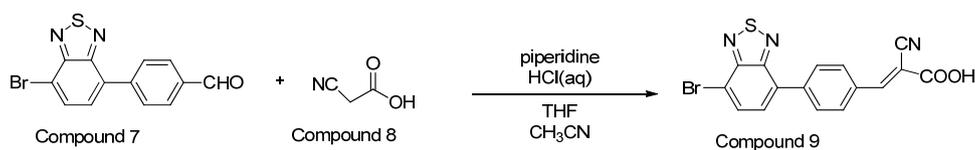
152 mg of compound 5 (M.W. = 810.10 g/mol, 0.188 mmol, 1.00 equiv.) was dissolved in 200 ml of THF/MeOH co-solvent (v/v = 1/1), followed by adding 20 ml of 8.33M $\text{NaOH}_{(\text{aq})}$. The reaction was stirred under reflux for 1 hour. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. 100 ml of ddH_2O was added in the residue, then conc. $\text{HCl}_{(\text{aq})}$ was added to neutralize the solution until $\text{pH} = 5$. The precipitation was collected by filtration, then purified by column chromatography (silica gel) using $\text{CH}_2\text{Cl}_2/\text{MeOH} = 9/1$ as eluent, followed by crystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give AN-11 (gold gray solid, 131mg, yield: 88%). ^1H -NMR (d_6 -DMSO at 2.50 ppm, 300 MHz); δ_{H} (ppm): 8.90 (d, $J = 8.4$ Hz, 2H); 8.65 (d, $J = 8.3$ Hz, 2H); 8.29 (d, $J = 7.6$ Hz, 1H); 8.20 (d, $J = 8.5$ Hz, 2H); 8.12 (d, $J = 8.5$ Hz, 2H); 8.06 (d, $J = 7.5$ Hz, 1H); 7.9-7.72 (m, 4H); 7.60 (d, $J = 8.4$ Hz, 2H); 6.71 (d, $J = 8.8$ Hz, 2H); 1.54 (s, 4H); 1.28 (d, $J = 11.4$ Hz, 20H); 0.85 (d, $J = 6.3$ Hz, 6H). Elemental Analysis: calcd for $\text{C}_{53}\text{H}_{53}\text{N}_3\text{O}_2\text{S} \cdot 0.5\text{H}_2\text{O}$: C 79.07%, H 6.76%, N 5.22%; found: C 79.20%, H 6.74%, N 5.23%. MALDI-TOF: calc'd for M^+ 795.39 ; found 795.42 [M] $^+$.



Compound 7

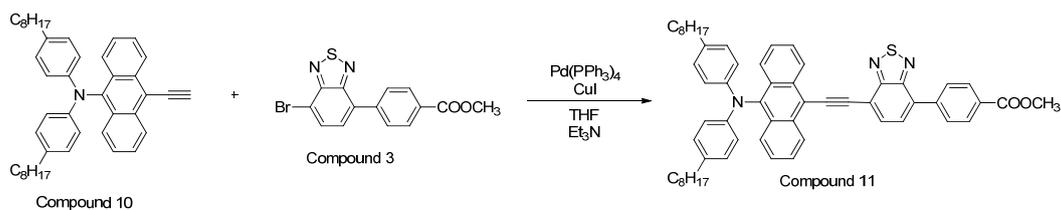
300 mg of compound 1 (M.W. = 293.96 g/mol, 1.021 mmol, 1.00 equiv.) was mixed

with 153 mg of compound 6 (M.W. = 149.94 g/mol, 10.17mmol, 1.00 equiv.) in 130 ml of toluene/THF co-solvent (v/v, 3/10). The mixture was then degassed by nitrogen bubble and sonic, followed by adding 118 mg of Pd(PPh₃)₄ (M.W. = 1155.56, 0.102 mmol, 0.01 equiv.). The reaction was stirred under reflux for 18 hours. The completion of the reaction was monitored by TLC. After cooled down, the solvent was removed with rotary evaporation. The residue was re-dissolved in ethyl acetate for washing with NH₄Cl_(aq). After drying over Na₂SO₄, the solvent was removed with rotary evaporation. The residue was purified on a column chromatograph (silica gel, eluent CH₂Cl₂/MeOH = 9/1) to give compound 7 (147mg, yield: 45%). ¹H-NMR (CDCl₃ at 7.26 ppm, 300 MHz): δ_H(ppm): 10.12 (s, 1H), 8.07 (q, J = 8.4 Hz, 4H), 7.98(d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H).



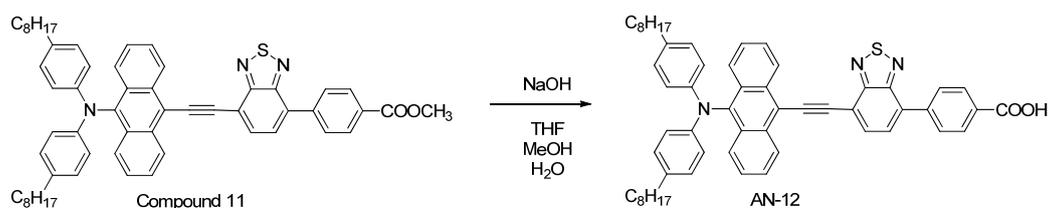
Compound 9

385 mg of compound 7 (M.W. = 319.18 g/mol, 0.156 mmol, 1.00 equiv.) was mixed with 311 mg of compound 8 (M.W. = 86.06 g/mol, 0.468 mmol, 3.00 equiv.) in 70 ml of THF/CH₃CN co-solvent (v/v, 5/2), followed by adding 0.1 ml of piperidine. The reaction was stirred under nitrogen atmosphere and refluxed for 13 hours. After cooled down, 5 ml of 3M HCl_(aq) was added in the mixture, then stirred for 30 mins. The completion of the reaction was monitored by TLC. The solvent was removed with rotary evaporation. The residue was re-dissolved in CH₂Cl₂ for washing with NH₄Cl_(aq). After drying over Na₂SO₄, the solvent was removed with rotary evaporation. The residue was purified on a column chromatograph (silica gel, eluent CH₂Cl₂/MeOH = 9/1) to give compound 9 (264 mg, yield: 57%). ¹H-NMR (d₆-DMSO at 2.50 ppm, 300 MHz): δ_H(ppm): 8.11 (m, 6H), 7.89 (d, J = 7.6 Hz, 1H).



Compound 11

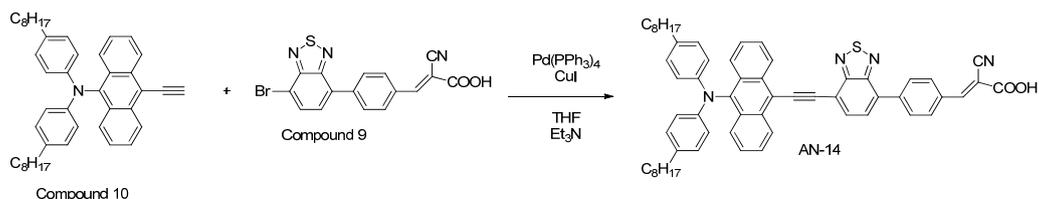
233 mg of compound 10 (M.W. = 593.88 g/mol, 0.392 mmol, 1.00 equiv.)^{S2} was mixed with 123 mg of compound 3 (M.W. = 349.20 g/mol, 0.353 mmol, 0.90 equiv.) in 35 ml of THF and 5 ml of Et₃N. After 3 cycles of freeze–pump–thaw, 5 mol % of Pd(PPh₃)₄ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 45°C for 46 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH₂Cl₂ for NH₄Cl_(aq) washes. After dried over Na₂SO₄, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/n-hexanes = 1/5 as eluent to give compound 11 (269mg, yield: 88%). ¹H-NMR (CDCl₃ at 7.26 ppm, 300 MHz): δ_H(ppm): 8.98 (d, *J* = 8.9 Hz, 2H), 8.31 – 8.05 (m, 7H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 6.97 (s, 8H), 3.99 (s, 3H), 2.48 (t, *J* = 7.8 Hz, 4H), 1.54 (s, 4H), 1.25 (s, 20H), 0.87 (s, 6H).



AN-12

269 mg of the compound 11 (MW = 862.17 g/mol, 0.312 mmol, 1.00 equiv.) was dissolved in 100 ml of THF/MeOH co-solvent (v/v = 3/1). After adding 30 mL of 8.33 M NaOH(aq), the solution was stirred at 50 °C for 3 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH₂Cl₂ for NH₄Cl_(aq) washes. After dried over Na₂SO₄, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using MeOH/CH₂Cl₂ = 1/9 as eluent to give AN-12 (M.W. = 848.15 g/mol, yield = 54 %). ¹H-NMR (d₆-DMSO at 2.50 ppm, 300 MHz): δ_H(ppm): 8.99 (d, *J* = 8.7 Hz, 2H); 8.42 (d, *J* = 7.3 Hz, 1H); 8.19-8.10 (m, 7H);

7.80 (t, $J = 6.8$ Hz, 2H); 7.60 (t, $J = 7.7$ Hz, 2H); 7.02 (d, $J = 8.3$ Hz, 2H); 6.87 (d, $J = 8.2$, 4H); 1.79-1.23 (m, 24H); 0.84 (t, $J = 6.3$ Hz, 6H). Elemental Analysis: calc'd for $C_{57}H_{57}N_3O_2S \cdot 0.5H_2O$: C 79.87%, H 6.82%, N 4.90%; found: C 79.60%, H 6.78%, N 4.83%. MALDI-TOF: calc'd for M^+ 847.42; found 848.15 $[MH]^+$



AN-14

230 mg of compound 10 (M.W. = 593.88 g/mol, 0.387 mmol, 1.00 equiv.) was mixed with 135 mg of compound 9 (M.W. = 386.22 g/mol, 0.349 mmol, 0.90 equiv.) in 35 ml of THF and 5 ml of Et_3N . After 3 cycles of freeze-pump-thaw, 5 mol % of $\text{Pd(PPh}_3)_4$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 45°C for 48 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $\text{NH}_4\text{Cl}_{(\text{aq})}$ washes. After dried over Na_2SO_4 , the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/n-hexanes = 1/9 as eluent to give AN-14 (103 mg, yield: 33%). $^1\text{H-NMR}$ (d_6 -DMSO at 2.50 ppm, 300 MHz): δ_{H} (ppm): 8.98 (d, $J = 8.7$ Hz, 2H), 8.42 (d, $J = 7.4$ Hz, 1H), 8.24 (d, $J = 7.8$ Hz, 2H), 8.15-8.02 (m, 6H), 7.79 (t, $J = 7.0$ Hz, 2H), 7.59 (t, $J = 7.1$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 4H), 6.87 (d, $J = 8.0$ Hz, 4H), 1.49-1.23 (d, 28H), 0.83(s, 6H) Elemental Analysis: calc'd for $C_{60}H_{58}N_4O_2S \cdot 3 H_2O$: C 75.60%, H 6.77%, N 5.88%; found: C 75.08%, H 6.39%, N 5.56%. MALDI-TOF: calc'd for M^+ 898.59; found 898.59 $[M]^+$

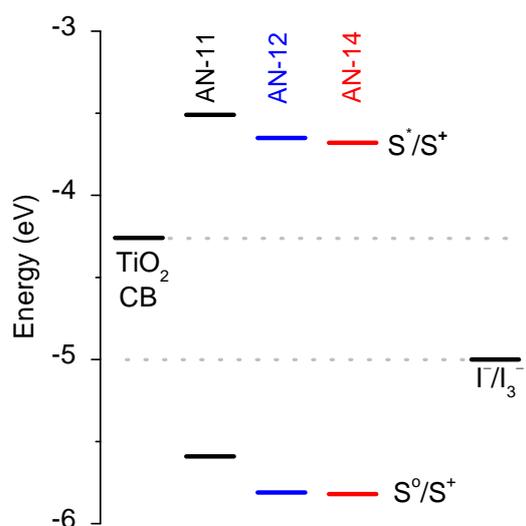


Fig. S1 Energy-level diagram of the AN dyes, comparing the ground-to-oxidized states (S^0/S^+), the first singlet excited-to-oxidized states (S^*/S^+) of each dye, the conduction bands (CB) of TiO₂, and the redox energy of the electrolyte. The first oxidation potentials were used to estimate the S^0/S^+ levels. The zero-zero excitation energies (E_{0-0}) obtained from the intersection of the corresponding normalized absorption and emission spectra were used to estimate the energy gaps between the S^*/S^+ and the S^0/S^+ levels.

Table S1 Small cell under indoor lights.^a

| Light source | Light intensity | Dye | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | (η %) |
|--------------|--|-------|--------------------------------|--------------|-----------|-------------|
| T5 | 1000 Lux (0.34 mW/cm ²) | AN-11 | 0.10±0.00 | 482.51±3.46 | 0.74±0.02 | 10.53±0.54 |
| | | AN-12 | 0.06±0.00 | 456.41±14.50 | 0.71±0.03 | 6.08±0.55 |
| | | AN-14 | 0.06±0.00 | 455.78±4.45 | 0.68±0.03 | 5.80±0.35 |
| LED | 1000 Lux (0.31 mW/cm ²) | AN-11 | 0.09±0.00 | 477.84±3.130 | 0.74±0.04 | 10.18±0.46 |
| | | AN-12 | 0.05±0.00 | 448.58±14.34 | 0.70±0.03 | 5.33±0.40 |
| | | AN-14 | 0.06±0.00 | 450.60±3.683 | 0.67±0.03 | 5.32±0.24 |

a. The small cells were not optimized for the measurements under indoor light. T5 fluorescent light and LED were manufactured by China Electric MFG. Co.

Fig. S2 Picture and dimension of the AN-11/R26 module. (active area = 26.8cm², aperture area = 28.4cm², total area = 38.5cm²)

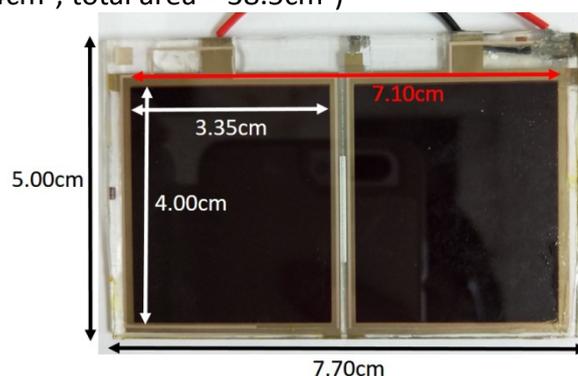


Table S2 Indoor PCE variation of the R26 modules based on different area dimensions.^{S3}

| Light source | Dye | Photon flux (lux) | η (%) (active area) ^a | η (%) (aperture area) ^b | η (%) (total area) ^c |
|--------------|-------|-------------------|---------------------------------------|---|--------------------------------------|
| T5 | AN-11 | 200 | 9.08 ±0.11 | 8.54 ±0.10 | 6.35±0.08 |
| | | 600 | 11.17 ±0.18 | 10.50 ±0.17 | 7.82±0.13 |
| | | 1000 | 11.94 ±0.16 | 11.22 ±0.15 | 8.36±0.11 |
| | Z907 | 200 | 8.69 ±0.04 | 8.17 ±0.04 | 6.08±0.03 |
| | | 600 | 10.70 ±0.08 | 10.06 ±0.08 | 7.49±0.06 |
| | | 1000 | 11.50 ±0.11 | 10.81 ±0.10 | 8.05±0.08 |
| LED | AN-11 | 200 | 9.68 ±0.13 | 9.10 ±0.12 | 6.78±0.09 |
| | | 600 | 10.95 ±0.17 | 10.29 ±0.16 | 7.66±0.12 |
| | | 1000 | 11.26 ±0.21 | 10.58 ±0.20 | 7.88±0.15 |
| | Z907 | 200 | 9.30 ±0.09 | 8.74 ±0.08 | 6.51±0.07 |
| | | 600 | 10.64 ±0.10 | 10.00 ±0.09 | 7.45±0.07 |
| | | 1000 | 10.91 ±0.11 | 10.26 ±0.10 | 7.63±0.07 |

^a. active area = 26.8 cm², ^b. aperture area = 28.4cm², ^c. total area = 38.5 cm².

Fig. S3 Picture and dimension of the AN-11/F17 module. (active area = 19.8cm², aperture area = 23.1cm², total area = 42.5cm²)

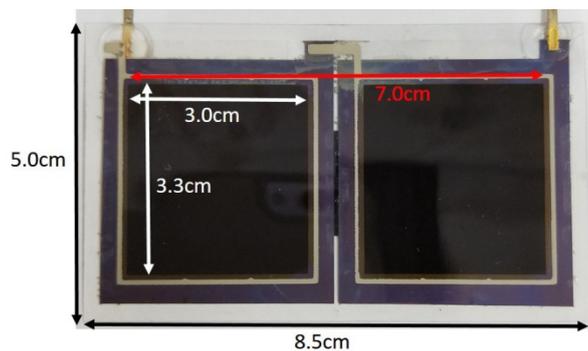


Table S3 Indoor PCE variation of the F17 modules based on different area dimensions.^{S3}

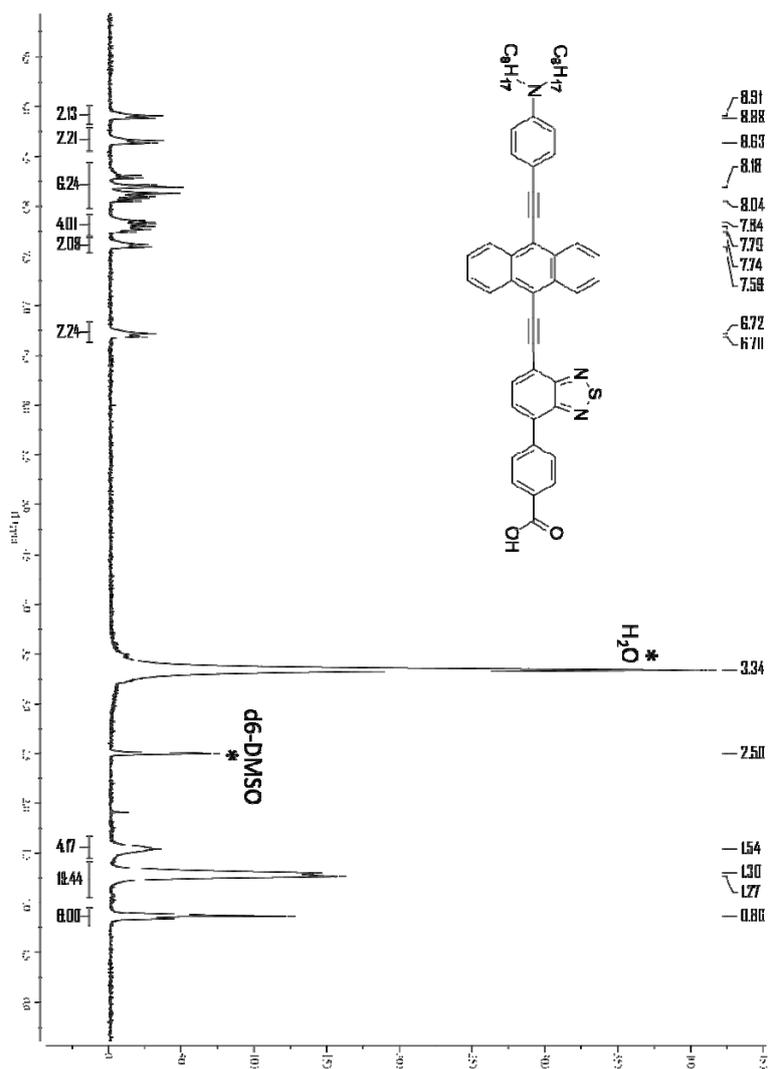
| Light source | Dye | Photon flux (lux) | η (%) (active area) ^a | η (%) (aperture area) ^b | η (%) (total area) ^c |
|--------------|-------|-------------------|---------------------------------------|---|--------------------------------------|
| T5 | AN-11 | 200 | 8.15±0.15 | 7.01±0.13 | 3.83±0.07 |
| | | 600 | 9.26±0.19 | 7.96±0.16 | 4.35±0.09 |
| | | 1000 | 9.60±0.16 | 8.26±0.14 | 4.51±0.08 |
| | Z907 | 200 | 7.92±0.19 | 6.81±0.16 | 3.72±0.09 |
| | | 600 | 9.13±0.09 | 7.85±0.08 | 4.29±0.04 |
| | | 1000 | 9.67±0.38 | 8.32±0.33 | 4.54±0.18 |
| LED | AN-11 | 200 | 8.08±0.18 | 6.95±0.15 | 3.80±0.08 |
| | | 600 | 9.37±0.19 | 8.06±0.16 | 4.40±0.09 |
| | | 1000 | 9.51±0.25 | 8.18±0.22 | 4.47±0.12 |
| | Z907 | 200 | 7.99±0.07 | 6.87±0.06 | 3.76±0.03 |
| | | 600 | 9.45±0.20 | 8.13±0.17 | 4.44±0.09 |
| | | 1000 | 9.98±0.11 | 8.58±0.09 | 4.69±0.05 |

^a active area = 19.8 cm², ^b aperture area = 23.1cm², ^c total area = 42.5 cm².

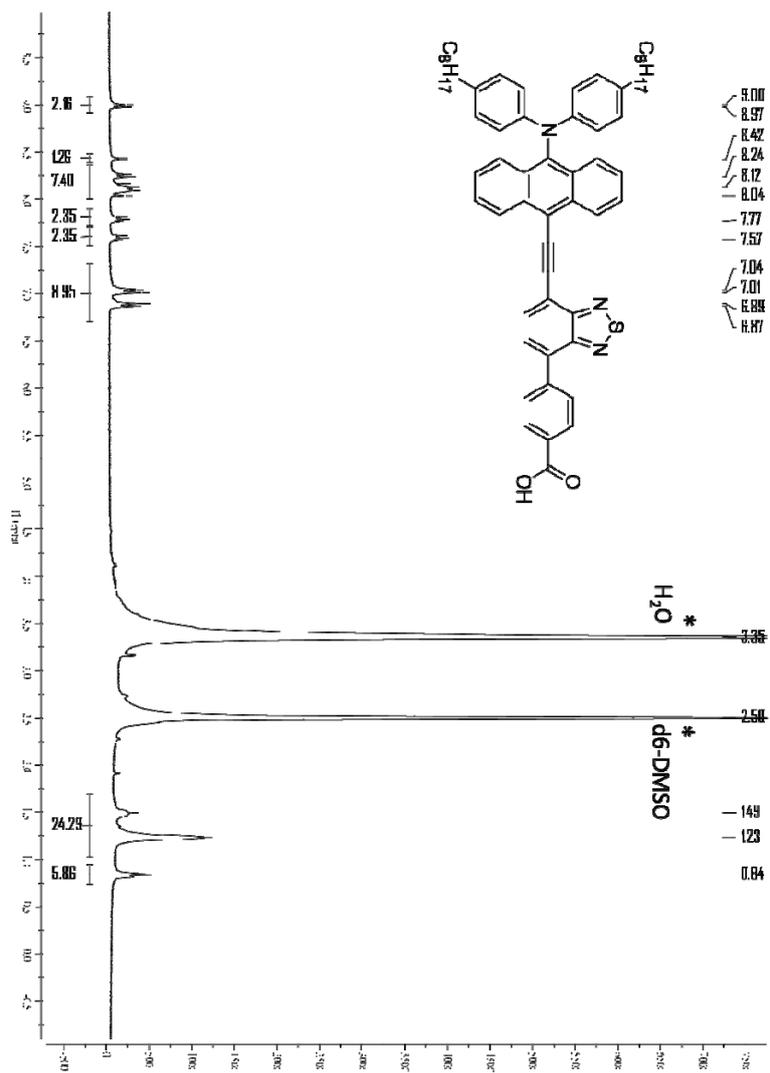
Reference

- S1. C.-L. Wang, P.-T. Lin, Y.-F. Wang, C.-W. Chang, B.-Z. Lin; H.-H. Kuo, C.-W. Hsu, S.-H. Tu, C.-Y. Lin, *J. Phys. Chem. C* 2015, **119**, 24282-24289.
- S2. C.-L. Wang, M. Zhang; Y.-H. Hsiao, C.-K. Tseng, C.-L. Liu, M. Xu, P. Wang, C.-Y. Lin, *Energy Environ. Sci.* 2016, **9**, 200-206.
- S3. A. Fakharuddin, R. Jose, T. M. Brown, F. Fabregat-Santiago, J. Bisquert, *Energy Environ. Sci.*, 2014, **7**, 3952-3981.

$^1\text{H-NMR}$ spectrum of AN-11



¹H-NMR spectrum of AN-12



¹H-NMR spectrum of AN-14

