Supporting Information

Efficient Anthryl Dye Enhanced by an Additional Ethynyl Bridge for Dye-Sensitized Module with Large Active Area to Drive Indoor Appliances

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Dye Synthesis and Characterization

(a).

Scheme S1. Synthesis of (a) AN-11 series and (b) AN-21 series of the dyes.
Compound 1

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\begin{array}{c}
\text{C}_3\text{H}_7
\end{array}
\]

Synthesis of the Compound 1 had been reported.\textsuperscript{51}

Compound 2

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\begin{array}{c}
\text{Br} - \text{N} - \text{S} - \text{O} - \text{O}
\end{array}
\]

200 mg of 3,5-Bis(methoxycarbonyl)benzeneboronic acid (M.W. = 238.00 g/mol, 0.84 mmol, 1.0 equiv.) mix with 494 mg of 4,7-Dibromobenzoo[c]-1,2,5-thiadiazole (M.W. = 293.96 g/mol., 1.68 mmol., 2.0 equiv.) and 546 mg of caesium carbonate (M.W. = 325.82 g/mol, 1.68 mmol., 2.0 equiv.) in 40 mL DMF. The mixture was then degassed by nitrogen bubbles and ultrasonication, followed by adding 98 mg of Pd(PPh\textsubscript{3})\textsubscript{4} (M.W. = 1155.56, 0.084 mmol, 0.01 equiv.). The reaction was stirred at 100°C for 20 hours. Completion of the reaction was monitored by TLC. After cooling down, the mixture was poured into dd-H\textsubscript{2}O to collect the precipitation by filtration. The collected solids were re-dissolved in ethyl acetate and washed with NH\textsubscript{4}Cl\textsubscript{(aq)}. After removing NH\textsubscript{4}Cl\textsubscript{(aq)} then drying over Na\textsubscript{2}SO\textsubscript{4}, the organic solvent was removed by rotary evaporation. The residue was purified on a column chromatograph (silica gel, 230-400 mesh, eluent: THF/n-hexanes = 1/5) to give compound 2 (light yellow solids, 187mg, yield: 55%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3} at 7.26 ppm, 300 MHz), δ\textsubscript{H}(ppm): 8.88 – 8.64 (m, 3H), 7.97 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 4.00 (s, 6H).

AN-11D-precursor

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\begin{array}{c}
\text{C}_3\text{H}_7
\end{array}
\]

175 mg of compound 1 (M.W. = 541.81 g/mol., 0.323 mmol., 1.00 equiv.) was mixed with 105 mg of compound 2 (M.W. = 407.24 g/mol, 0.258 mmol, 0.8 equiv.) in 35 ml of THF and 5 ml of Et\textsubscript{3}N. After 3 cycles of freeze–pump–thaw, 10 mol. % of Pd(PPh\textsubscript{3})\textsubscript{4} and Cul were added to the solution under an inert atmosphere. The reaction was stirred at 50°C for 40 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were redissolved in CH\textsubscript{2}Cl\textsubscript{2}. After NH\textsubscript{4}Cl\textsubscript{(aq)} washes, the organic layer was dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed by rotary evaporation. The residues were purified by column
chromatography (silica gel, 230-400 mesh, eluent: THF/n-hexanes = 1/3), followed by crystallization from CH₂Cl₂/MeOH to give AN-11D-precursor (dark red solids, 135 mg, yield: 63%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δH(ppm): 9.03 – 8.85 (m, 4H), 8.83 – 8.69 (m, 3H), 8.09 (d, J = 7.4 Hz, 1H), 7.89 (d, J = 7.4 Hz, 1H), 7.80 – 7.56 (m, 6H), 6.68 (d, J = 8.8 Hz, 2H), 4.02 (s, 6H), 3.41 – 3.26 (m, 4H), 1.63 (b, 4H), 1.38 – 1.22 (m, 20H), 1.00 – 0.85 (m, 6H).

**AN-11D**

60 mg of AN-11D-precursor (M.W. = 868.13 g/mol, 0.069 mmol, 1.00 equiv.) was dissolved in 40 ml of THF/MeOH (v/v = 3/1), followed by adding 1 ml of 8.33 M NaOH(aq). The reaction was stirred under reflux for 3 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. 100 ml of dd-H₂O was added to the residues, followed by adding conc. HCl(aq) to neutralize the solution to pH = 5. The precipitation was collected by filtration then purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH = 9/1). Crystallization from CH₂Cl₂/MeOH gives 25 mg of AN-11D (dark red solids, yield: 43%). ¹H-NMR (d₈-THF at 3.58, 1.73 ppm, 300 MHz), δH(ppm): 9.14 – 8.94 (m, 4H), 8.85 – 8.68 (m, 3H), 8.23 (d, J = 7.4 Hz, 1H), 8.08 (d, J = 7.4 Hz, 1H), 7.84 – 7.51 (m, 6H), 6.75 (d, J = 8.9 Hz, 2H), 3.48 – 3.29 (m, 4H), 1.66 (b, 4H), 1.50 – 1.23 (m, 20H), 1.02 – 0.81 (m, 6H). Elemental Analysis: calc’d for C₅₄H₅₃N₃O₄S·1.5H₂O: C, 74.80; H, 6.51; N, 4.85; found: C, 75.00; H, 6.23; N, 4.80. MALDI-TOF: calc’d for [M]⁺ 839.376; found 839.365.

**AN-11H-precursor**

200 mg of AN-11 (M.W. = 796.07 g/mol, 0.251 mmol, 1.00 equiv.) was mixed with 58 mg of N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDCI·HCl) (M.W. = 191.70 g/mol., 0.30 mmol., 1.2 equiv.) and 41 mg 1-hydroxybenzotriazole hydrate (M.W. = 135.12 g/mol., 0.30 mmol., 1.2 equiv.) in 50 ml of DMF, then stirred under R.T. for 20 min. After stirring for 20 min., 45 mg of O-(tetrahydro-2H-pyran-2-yl) hydroxylamine (M.W. = 117.15 g/mol., 0.38 mmol., 1.5 equiv.) was added into the mixture. The reaction was stirred under R.T. for 20 hours. Completion of the reaction was monitored by TLC. Upon completion, the mixture was poured into dd-H₂O to
collect the precipitation by filtration. The collected solids were re-dissolved in CH₂Cl₂ and then washed with NH₄Cl(aq). After removing NH₄Cl(aq) then drying over Na₂SO₄, the organic solvent was removed with rotary evaporation. The residue was purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH = 9/1), followed by crystallization from CH₂Cl₂/MeOH to give 210 mg of AN-11H-precursor (dark red solids, yield: 93%). ¹H-NMR (CDCl₃ at 7.26 ppm, 300 MHz), δH(ppm): 8.92 (d, J = 8.9 Hz, 3H, -NH), 8.72 (d, J = 8.4 Hz, 2H), 8.14 – 8.00 (m, 3H), 7.94 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 7.4 Hz, 1H), 7.75 – 7.58 (m, 6H), 6.68 (d, J = 8.9 Hz, 2H), 5.14 (s, 1H), 4.25 – 3.87 (m, 2H), 3.86 – 3.50 (m, 2H), 3.40 – 3.27 (m, 4H), 2.07 – 1.78 (m, J = 4.0 Hz, 4H), 1.65 (b, 4H), 1.41 – 1.28 (m, 20H), 0.99 – 0.84 (m, 6H).

AN-11H

200 mg of AN-11-precursor (M.W. = 895.20 g/mol., 0.223 mmol., 1.00 equiv.) was dissolved into 100 mL of mixed solvent (THF:H₂O:AcOH = 7:2:1). The solution was then degassed by nitrogen bubble and sonic for 30 min. The reaction was stirred under 60°C for 20 hours. The completion of the reaction was monitored by TLC. Upon completion, poured the mixture into water and collected the precipitation by filtration. The collected solids were re-dissolved in CH₂Cl₂ and washed with NaHCO₃(aq). After removing NH₄Cl(aq) then drying over Na₂SO₄, the solvent was removed with rotary evaporation. The residue was purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH/AcOH = 9/1/0.3. Crystallization from CH₂Cl₂/MeOH gives 104 mg of AN-11H (dark red solids, yield: 58%). ¹H-NMR (d₈-THF at 3.58, 1.73 ppm, 300 MHz), δH(ppm): 10.76 (b, 1H, -OH), 9.03 (d, J = 8.1 Hz, 2H), 8.75 (d, J = 8.3 Hz, 2H), 8.09 (b, 7H, -NH), 7.81 – 7.42 (m, 6H), 6.75 (d, J = 8.6 Hz, 2H), 3.47 – 3.28 (m, 4H), 1.66 (b, 4H), 1.47 – 1.23 (m, 20H), 1.01 – 0.79 (m, 6H). Elemental Analysis: calc'd for C₅₄H₅₃N₃O₄S·0.1H₂O: C, 76.78; H, 6.81; N, 6.76; found: C, 76.66; H, 6.77; N, 6.44. MALDI-TOF: calc'd for [M]⁺ 810.397; found 810.376.

Compound 3

200 mg of compound 2 (M.W. = 541.81 g/mol., 0.369 mmol., 1.0 equiv.) mix with 217 mg of 4,7-Dibromobenzo[c]-1,2,5-thiadiazole (M.W. = 293.96 g/mol., 0.738 mmol., 2.0
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 Cul were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50°C for 70 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂ for NH₄Cl(aq) washes. After removing NH₄Cl(aq) then during over Na₂SO₄, the solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: THF/n-hexanes = 1/8. Crystallization from CH₂Cl₂/MeOH gives 167 mg of Compound 3 (dark purple solids, yield: 59%). ¹H-NMR (CDCl₃ at 7.26 ppm, 300 MHz), δH(ppm): 8.81 (d, J = 8.4 Hz, 2H), 8.69 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 7.6 Hz, 1H), 7.73 – 7.55 (m, 7H), 6.67 (d, J = 8.7 Hz, 2H), 3.47 – 3.21 (m, 4H), 1.63 (b, 4H), 1.45 – 1.21 (m, 20H), 1.01 – 0.80 (m, 6H).

AN-21

50 mg of compound 3 (M.W. = 754.86 g/mol., 0.066 mmol., 1.0 equiv.) was mixed with 29 mg of 4-ethynylbenzoic acid (M.W. = 146.14 g/mol., 0.198 mmol., 3.0 equiv.) in 35 ml of THF and 5 ml of Et₃N. After 3 cycles of freeze−pump−thaw, 20 mol % of Pd(PPh₃)₄ and Cul were added to the solution under an inert atmosphere. The reaction was stirred at 50°C for 48 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂ for NH₄Cl(aq) washes. After removing NH₄Cl(aq) then during over Na₂SO₄, the solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH = 9/1. Crystallization from THF/MeOH gives 41 mg of AN-21 (dark gray solids, yield: 76%). ¹H NMR (d₈-THF at 3.58, 1.73ppm, 300 MHz) δH(ppm): 8.99 (d, J = 8.4 Hz, 2H), 8.75 (d, J = 8.5 Hz, 2H), 8.11 (t, J = 7.2 Hz, 3H), 7.97 (d, J = 7.4 Hz, 1H), 7.83 – 7.53 (m, 8H), 6.75 (d, J = 8.8 Hz, 2H), 3.46 – 3.35 (m, 4H), 1.66 (b, 4H), 1.45 – 1.24 (m, 20H), 1.01 – 0.82 (m, 6H). Elemental Analysis: calc’d for C₅₁H₄₁N₃O₄S・1.5H₂O: C, 77.98; H, 6.66; N, 4.96; found: C, 77.98; H, 6.74; N, 5.15. MALDI-TOF: calc’d for [M⁺] 819.386; found 819.377

Compound 4

200 mg of compound 3 (M.W. = 754.86 g/mol., 0.265 mmol., 1.0 equiv.) was mixed
with 0.6 mL (trisopropylsilyl)acetylene (d = 0.813 g/mL, 182.38 g/mol., 2.67 mmol., 10 equiv.) in 35 ml of THF and 5 ml of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol % of Pd(PPh₃)₄ and Cul were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50°C for 20 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂ for NH₄Cl(aq) washes. After removing NH₄Cl(aq) then during over Na₂SO₄, the solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/Hexane = 1/3. Crystallization from CH₂Cl₂/MeOH gives 200mg of Compound 4 (dark purple solids, yield: 88%). ¹H-NMR (CDCl₃ at 7.26 ppm, 300 MHz), δH(ppm): 8.92 (d, J = 8.4 Hz, 2H), 8.73 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 7.4 Hz, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.76 – 7.56 (m, 6H), 6.68 (d, J = 7.4 Hz, 2H), 3.48 – 3.21 (m, 4H), 1.63 (b, 4H), 1.47 – 1.26 (m, 20H), 1.25 – 1.08 (m, 21H), 0.99 – 0.79 (m, 6H).

AD-21D-precursor

184 mg of compound 4 (M.W. = 856.33 g/mol., 0.214 mmol., 1.0 equiv.) was dissolve in 100 mL THF, then 0.6 mL, 1M TBAF solution was added into the reaction under dark, 0°C, stir for one hour. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂ for NH₄Cl(aq) washes. After dried over Na₂SO₄, the solvent was removed by rotary evaporation. The residue (150mg) was directly go to next step without further purification. The residues 150 mg (M.W. = 699.988 g/mol., 0.214 mmol., 1.0 equiv.) was mix with 137mg Dimethyl 5-bromoisophthalate (M.W. = 273.08 g/mol., 0.500 mmol., 2.3 equiv.) in 50 ml of THF and 10 ml of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol % of Pd(PPh₃)₄ and Cul were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50°C for 20 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂ for NH₄Cl(aq) washes. After removing NH₄Cl(aq) then during over Na₂SO₄, the solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: THF/Hexane = 1/3. Crystallization from CH₂Cl₂/MeOH gives 134mg of AD-21D-precursor (black solids, yield: 70%). ¹H-NMR (CDCl₃ at 7.26 ppm, 300 MHz), δH(ppm): 8.91 (d, J = 8.4 Hz, 2H), 8.80 – 8.64 (m, J = 13.4, 4.9 Hz, 3H), 8.52 (d, J = 1.5 Hz, 2H), 7.98 (d, J = 7.4 Hz, 1H), 7.89 (d, J = 7.4 Hz, 1H), 7.78 – 7.57 (m, 6H), 6.67 (d, J = 8.6 Hz, 2H), 3.99 (s, 6H), 3.46 – 3.25 (m, 4H), 1.63 (s, 4H), 1.43 – 1.24 (m, 20H), 0.99 – 0.79 (m, 6H), 1.25 – 1.08 (m, 21H), 0.99 – 0.79 (m, 6H).
0.90 (t, J = 6.4 Hz, 6H).

**AN-21D**

60 mg of AN-21D-precursor (M.W. = 892.16 g/mol., 0.067 mmol., 1.00 equiv.) was dissolved in 50 ml of THF/MeOH co-solvent (v/v = 4/1), followed by adding 1 ml of 8.33 M NaOH(aq). The reaction was stirred under reflux for 3 hours. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. 100 ml of ddH2O was added in the residue, then conc. HCl(aq) was add to neutralize the solution until pH = 5. The precipitation was collected by filtration, then purified by column chromatography (silica gel, 230-400 mesh, eluent: CH2Cl2/MeOH = 9/1. Crystallization from CH2Cl2/MeOH gives 41mg AN-11D (black solids, yield: 70%).

1H NMR (d8-THF at 3.58, 1.73ppm, 300 MHz) δH(ppm): 8.83 (d, J = 8.7 Hz, 2H), 8.59 (d, J = 8.5 Hz, 2H), 8.48 (s, 1H), 8.30 (s, 2H), 8.11 (d, J = 7.5 Hz, 1H), 8.01 (d, J = 7.4 Hz, 1H), 7.93 – 7.66 (m, 4H), 7.56 (d, J = 8.3 Hz, 2H), 6.65 (d, J = 8.7 Hz, 2H), 1.53 (b, 4H), 1.39 – 1.16 (m, 20H), 0.91 – 0.82 (m, 6H). Elemental Analysis: calc’d for C56H53N3O4S·0.5H2O: C, 77.03; H, 6.23; N, 4.81; found: C, 76.78; H, 6.25; N, 4.66. MALDI-TOF: calc’d for [M+] 863.376; found 863.880

**AN-21H**

140 mg of compound 4 (M.W. = 856.33 g/mol., 0.163 mmol., 1.0 equiv.) was dissolve in 100 mL THF, then 0.5 mL, 1M TBAF solution was added into the reaction under dark, 0°C, stir for one hour. 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 removing NH4Cl(aq) then during over Na2SO4, the solvent was removed by rotary evaporation. The residues (113mg) were directly go to next step without further purification. The residues 113 mg (M.W. = 699.988 g/mol, 0.161 mmol, 1.0 equiv.) were mix with 128 mg N-Hydroxy-4-iodobenzamide52 (M.W. = 263.03 g/mol, 0.487 mmol, 3.0 equiv.) in 60 ml of THF and 5 ml of Et3N. After 3 cycles of freeze–pump–thaw, 30 mol % of Pd2(dba)3 and 2.4eq AsPh3 were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 60°C for 20 hours. The completion of the reaction was monitored by TLC.
Upon completion, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH/AcOH = 9/1/0.3. Crystallization from CH₂Cl₂/MeOH gives 85mg of AD-21H (dark red solids, yield: 63%). ¹H-NMR (d₈-THF at 3.58, 1.73ppm, 300 MHz), δH(ppm): 10.80 (b, 1H, -OH), 8.99 (d, J = 6.3 Hz, 2H), 8.75 (d, J = 7.9 Hz, 2H), 8.32 – 7.19 (m, 13H, -NH), 6.75 (d, J = 8.1 Hz, 2H), 3.40 (b, 5H), 1.66 (b, 4H), 1.48 – 1.21 (m, 20H), 1.01 – 0.84 (m, 6H). Elemental Analysis: calc’d for C₅₅H₅₄N₄O₂S·0.5H₂O: C, 76.62; H, 6.66; N, 6.50; found: C, 76.28; H, 6.54; N, 6.22. MALDI-TOF: calc’d for [M⁺] 834.397; found 834.364
NMR spectra:
AN-11D

Figure S1. H\textsuperscript{1}-NMR spectrum of AN-11D.
Figure S2. H1-NMR spectrum of AN-11H
Figure S3. H$^1$-NMR spectrum of AN-21
Figure S4. H¹-NMR spectrum of AN-21D
Figure S5. H$^1$-NMR spectrum of AN-21H
Figure S6. Stability of (a) AN-small cells, and (b) AN-21 module. As shown in Figure S6b, the changes in PCE of AN-21 module is consistent with the change in the $V_{oc}$. 
Figure S7. Sintering program for cathode.

Figure S8. (a) Pre-sintering program and (b) post-sintering program for anode.
Figure S9. (a) Dimension of the DSC-driven remote controller and , (b) – (d) the charging test.
**Figure S10.** Observation chamber, good for watching plants or being used as an ant‐farm. This device is powered by four AN-21 modules. The electronic paper displays the humidity and temperature inside the chamber. An LED light (inside the chamber, not shown) provides illumination.

**Figure S11.** Four views of a static cancelling comb, powered by one AN-21 module.
Figure S12. FT-IR spectra of the AN-dyes/KBr.

AN-11: 3436, 2922, 2851, 2170, 1677, 1603, 1517, 1368, 1298, 1186, 770, 639 (cm⁻¹).
AN-11D: 3438, 2922, 2855, 2170, 1683, 1602, 159, 1397, 1368, 1263, 1184, 763, 638 (cm⁻¹).
AN-11H: 3428, 2922, 2852, 2175, 1603, 1519, 1395, 1369, 1185, 763, 638 (cm⁻¹).
AN-21: 3434, 2922, 2851, 2169, 1683, 1603, 1518, 1367, 1288, 1185, 766, 638 (cm⁻¹).
AN-21D: 3435, 2925, 2853, 2172, 1695, 1604, 1520, 1369, 1398, 1277, 1186, 764, 639 (cm⁻¹).
AN-21H: 3435, 2923, 2852, 2171, 1604, 1519, 1395, 1367, 1187, 762, 637 (cm⁻¹).
Reference