ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for *Adv. Funct. Mater.*, DOI: 10.1002/adfm.201101961

Organic Dye Design Tools for Efficient Photocurrent Generation in Dye-Sensitized Solar Cells: Exciton Binding Energy and Electron Acceptors

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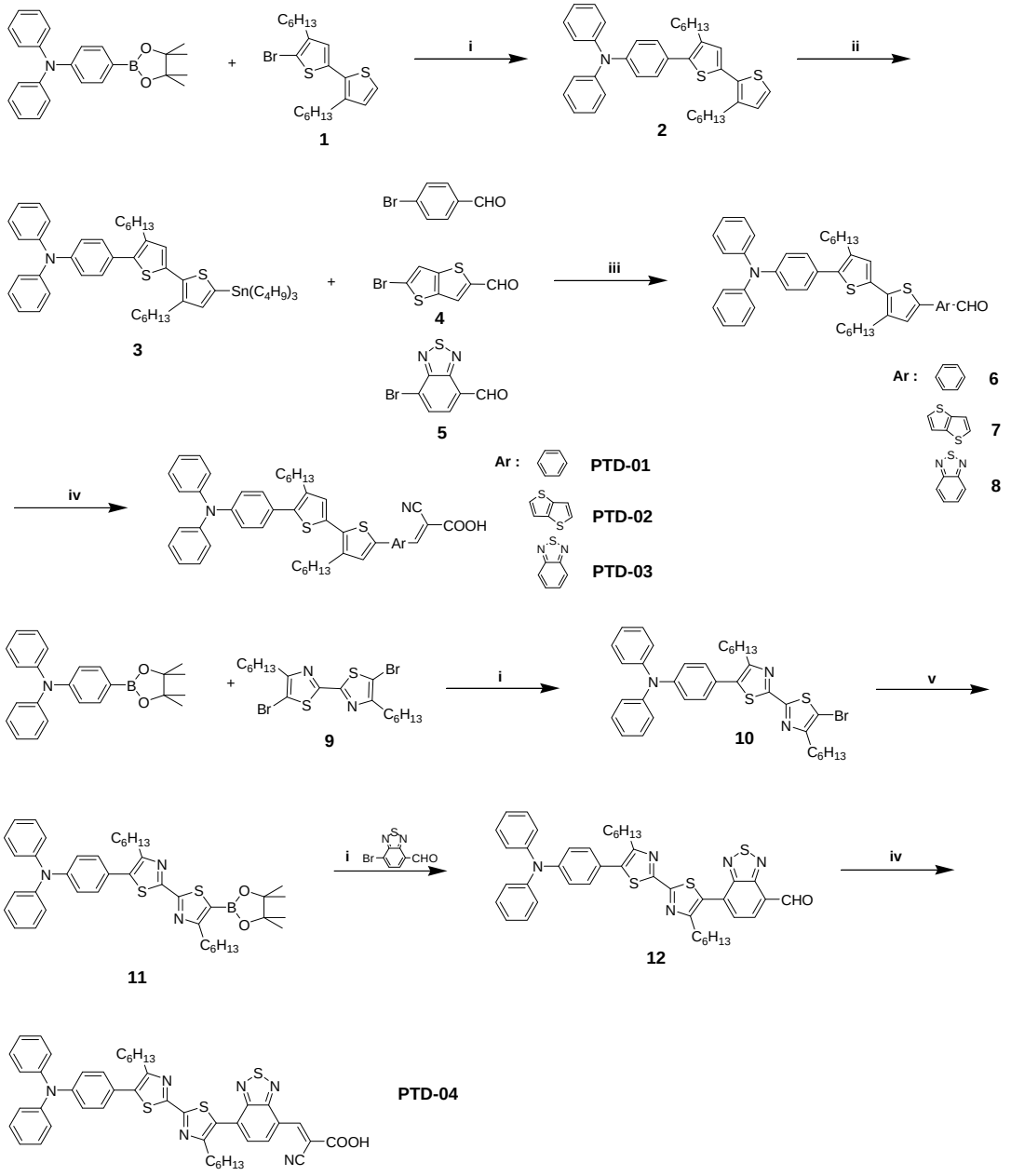
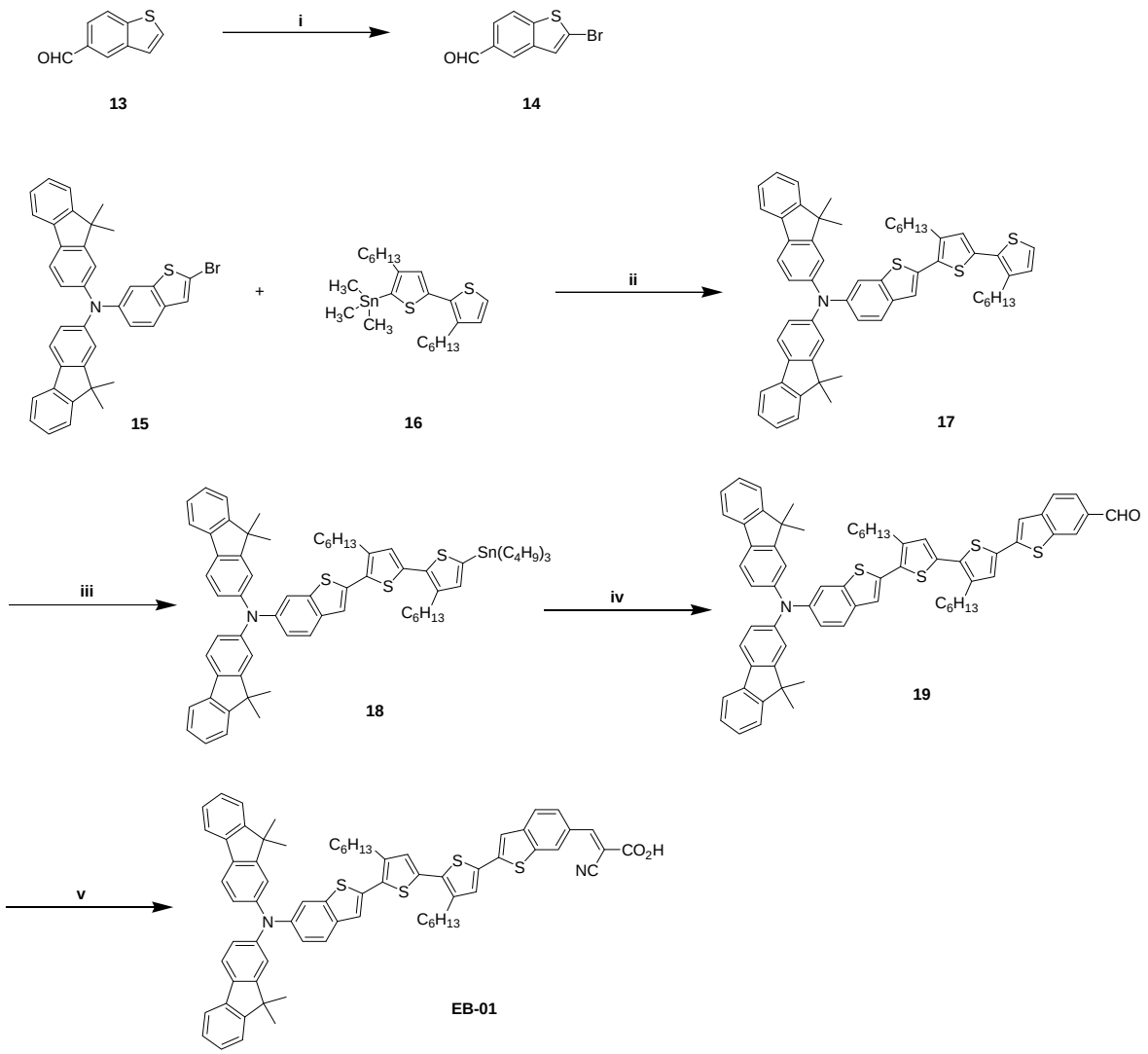
By *Bong-Gi Kim, Chang-Gua Zhen, Eun Jeong Jeong, John Kieffer,* and Jinsang Kim**



Scheme S1. Chemical structures and synthetic routes of prototype dyes. i) Na_2CO_3, Pd(0), DMF, 120 ^oC, 12 hours; ii) n-BuLi, $Sn(C_4H_9)_3Cl$, THF, -70 ^oC; iii) Pd(0), THF, reflux, 12 hours; iv) cyanoacetic acid, piperidine, acetonitrile, reflux, 6 hours; v) n-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxa-borolane, THF, -70 ^oC.



Scheme S2. Chemical structures and synthetic routes of EB-01. i) LDA, Br_2, THF; ii) Pd(0), THF, reflux, 12 hours; iii)) n-BuLi, $Sn(C_4H_9)_3Cl$, THF, -70 ^oC; iv) 14, Pd(0), THF, reflux, 12 hours; v) cyanoacetic acid, piperidine, acetonitrile, reflux, 6 hours.

Synthesis. As shown in Scheme S1 and Scheme S2, four different prototype dyes and EB-01 were synthesized. All starting materials were purchased from commercial supplier (Aldrich and Fisher Sci.). Synthesized compounds were fully characterized with ^1H NMR and GC-mass. Compound **1**, **5**, **9, 13, 15, 16** were prepared as previously described manner.[1-6]

General procedure of Suzuki type coupling. Under inert conditions (Ar), aromatic bromide, boronic ester derivatives (1.1 eq.) and Pd(0) (4 mol%) were dissolved in DMF. Then, the mixture was heated up to 60 ^oC and 1 M Na_2CO_3 was added. After stirring at 120 ^oC for 12 hours, the mixture was poured into water and extracted with chloroform. The organic solution was dried with $MgSO_4$ and evaporated. The residue was purified with column chromatography.

Compound (2). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.29 (m, 3H), 7.15 (m, 7H), 7.07 (t, 2H), 7.02 (s, 1H), 6.95 (d, 1H), 2.84 (t, 2H), 2.71 (t, 2H), 1.68 (m, 4H), 1.35 (m, 12H), 0.92 (m, 6H), and m/z EIMS 578.

*Compound (**10**).* ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.64 (d, 2H), 7.20-7.40 (m, 4H), 7.00-7.20 (m, 8H), 2.78 (t, 4H), 1.68 (m, 4H), 1.46 (m, 12H), 0.85 (t, 6H), and m/z EIMS 659.

*Compound (**12**).* ^{1}H-NMR (400MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.31 (d, 1H), 7.87 (d, 1H), 7.22-7.40 (m, 6H), 7.00-7.20 (m, 8H), 2.82-2.93 (m, 4H), 1.76-1.85 (m, 4H), 1.24-1.30 (m, 12H), 0.83-0.89 (t, 6H), and m/z EIMS 742.

*Compound (**3**).* To a solution of **2** (1 mmol) in THF (50 mL) was added dropwise n-BuLi (1.2 mmol, 2.5 M in hexane) at -70 ^{o}C under Argon conditions. The reaction was kept at -70 ^{o}C for 30 min and then tributyltinchloride (1.2 mmol) was added. The mixture was warmed to room temperature and stirred overnight. After pouring the mixture into water, the organic layer was separated; the aqueous layer was extracted with ether, and the combined organic layers were dried with $MgSO_4$. After evaporating the solvent, the residue was chromatographically purified on deactivated silica gel eluting with n-hexane to afford the products **(3)** as a yellowish oil, which were used for the following reactions without further purification.

*5-bromothieno[3,2-b]thiophene-2-carbaldehyde (**4**).* To a solution of 2,5-dibromothieno[3,2-b]thiophene (0.1 mmol) in THF was added dropwise n-BuLi (0.05 mmol, 2.5 M in hexane) at -70 ^{o}C under Argon conditions. The reaction was kept at -70 ^{o}C for 30 min and then anhydrous DMF (0.05 mmol) was added. The mixture was warmed to room temperature and stirred overnight. After pouring the mixture into water, the organic layer was separated; the aqueous layer was extracted with ether, and the combined organic layers were dried with $MgSO_4$. After evaporating solvent, the residue was chromatographically purified on silica gel eluting with ethylacetate/hexane (1/5) to afford the products **(4)** as a yellowish powder. ^{1}H-NMR (400MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.84 (s, 1H), 7.35 (s, 1H), and m/z EIMS 247.

General procedure of Stille type coupling. Under inert conditions (Ar), aromatic bromide, tributyltin derivatives (1.1 eq) and Pd(0) (1 mol%) were dissolved in anhydrous THF. Then, the mixture was heated up to 80 ^{o}C and stirred for 8 hours. After cooling to room temperature, the mixture was poured into water and extracted with chloroform. The organic solution was dried with $MgSO_4$ and evaporated. The residue was purified with column chromatography.

*Compound (**6**).*^{1}H-NMR (400MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.81 (d, 2H), 7.67 (d, 2H), 7.22-7.40 (m, 6H), 6.85-7.20 (m, 10H), 2.60-2.80 (m, 4H), 1.76-1.85 (m, 4H), 1.24-1.30 (m, 12H), 0.83-0.89 (t, 6H), and m/z EIMS 683.

*Compound (**7**).*^{1}H-NMR (400MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.82 (s, 2H), 7.65 (m, 2H), 7.20-7.40 (m, 7H), 6.88-7.18 (m, 8H), 2.62 (t, 2H), 2.68 (t, 2H), 1.78-1.85 (m, 4H), 1.24-1.30 (m, 12H), 0.83-0.89 (t, 6H), and m/z EIMS 744.

*Compound (**8**).* ^{1}H-NMR (400MHz, $CDCl_3$) δ 10.65 (s, 1H), 8.00-8.15 (m, 2H), 7.20-7.40 (m, 6H), 6.88-7.20 (m, 10H), 2.64 (t, 2H), 2.70 (t, 2H), 1.78-1.85 (m, 4H), 1.24-1.30 (m, 12H), 0.83-0.89 (t, 6H), and m/z EIMS 741.

*Compound (**17**).* ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.65 (t, 2H), 7.58 (d, 2H), 7.41 (d, 2H), 7.35 (t, 2H), 7.30-7.24 (m, 6H), 7.23 (s, 2H), 7.20-7.14 (m, 2H), 7.15 (br, 1H), 7.11 (br, 1H), 6.94 (s, 1H), 2.78 (t, 2H), 2.72 (t, 2H), 1.68-1.51 (m, 4H), 1.42 (s, 12H), 1.38-1.14(m, 12H), 0.88 (t, 3H), 0.76 (t, 3H) and m/z EIMS 867.

*Compound (**19**).* ^{1}H-NMR (400MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.42 (s, 1H), 7.95 (d, 1H), 7.76 -7.62 (m, 5H), 7.51 (d, 2H), 7.47-7.28 (m, 8H), 7.24-7.14 (m, 5H), 6.99(s, 1H), 6.94 (s, 1H), 2.80 (t, 2H), 2.74(t, 2H), 1.68-1.51 (m, 4H), 1.42 (s, 12H), 1.38-1.14(m, 12H), 0.92-80 (m, 6H) and m/z EIMS 1027.

*Compound (**11**).* Under inert conditions (Ar), compound 10 (1.0 mmol) was dissolved into anhydrous THF and 2.5M BuLi (0.4 ml) was added dropwise at -70 ^{o}C. After further stirring for 1 hour, bis(pinacolato)diboron (0.28 g. 1.1 eq) was added and warmed to room temperature. The mixture was additionally stirred overnight and poured into water. After extraction with chloroform, the organic layer was dried with $MgSO_4$. After evaporating off the solvent in vacuo, the residue was purified with column chromatography. ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.20-7.31 (m. 7H), 7.03-7.16 (m, 9H), 3.02 (t, 2H), 2.82 (t, 2H), 1.72-1.77 (m, 4H), 1.30-1.37 (m, 24H).0.88 (t, 6H), and m/z EIMS 707.

*Compound (**14**).* Under inert condition (Ar), LDA (3.39 ml, 2.0 M solution in THF/heptane/ethylbenzene) was added into **13** (1.0 g, 6.2 mmol) solution in anhydrous THF (50 ml) at 0 ^{o}C. After stirring the mixture for additional 1 hour under room temperature, bromine (1.08 g, 6.78 mmol) was added dropwise under ice bath and the solution was stirred for 3 hours under room temperature. Then, saturated sodium bisulfate solution was added and the solution was extracted with chloroform. After drying the extracted solution with $MgSO_4$, the solvent was evaporated. The product **14** was obtained by silica gel chromatography with eluent (MC/Hexane; 1:5) in 75% yield. ^{1}H-NMR (400MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.54 (s, 1H), 8.00 (d, 1H), 7.96 (d, 1H), 7.80 (s, 1H) and m/z EIMS 242.

*Compound (**18**).* To a solution of **17** (1 mmol) in THF (50 mL) was added dropwise n-BuLi (1.2 mmol, 2.5 M in hexane) at -70 ^{o}C under Argon conditions. The reaction was kept at -70 ^{o}C for 30 min and then tributyltinchloride (1.2 mmol) was added. The mixture was warmed to room temperature and stirred overnight. After pouring the mixture into water, the organic layer was separated; the aqueous layer was extracted with ether, and the combined organic layers were dried with $MgSO_4$. After evaporating the solvent, the residue was chromatographically purified on deactivated silica gel eluting with n-hexane to afford the products **(18)** as yellowish oil, which were used for the following reactions without further purification.

General procedure of introducing cyanoacetic acid. Aldehyde containing compound, cyanoacetic acid (2.0 eq.), and piperidine (1.0 eq.) were dissolved into acetonitrile/chloroform

(v/v, 8/2). The mixture was refluxed for 6 hours and the solvent was evaporated off in vacuo. The residue was purified with column chromatography.

PTD-01. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.86 (d, 2H), 7.70 (d, 2H), 7.26-7.46 (m, 6H), 6.86-7.24 (m, 10H), 2.61-2.84 (m, 4H), 1.77-1.88 (m, 4H), 1.25-1.32 (m, 12H), 0.82-0.90 (t, 6H), and m/z EIMS 750.

PTD-02. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.86 (s, 2H), 7.68 (m, 2H), 7.24-7.42 (m, 7H), 6.90-7.20 (m, 8H), 2.63 (t, 2H), 2.69 (t, 2H), 1.80-1.86 (m, 4H), 1.25-1.32 (m, 12H), 0.84-0.90 (t, 6H), and m/z EIMS 812.

PTD-03. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.01-8.16 (m, 2H), 7.19-7.39 (m, 6H), 6.89-7.22 (m, 10H), 2.63 (t, 2H), 2.71 (t, 2H), 1.78-1.84 (m, 4H), 1.24-1.31 (m, 12H), 0.84-0.89 (t, 6H), and m/z EIMS 807.

PTD-04. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.32 (d, 1H), 7.89 (d, 1H), 7.24-7.41 (m, 6H), 7.02-7.21 (m, 8H), 2.82-2.92 (m, 4H), 1.75-1.86 (m, 4H), 1.25-1.32 (m, 12H), 0.84-0.89 (t, 6H), and m/z EIMS 810.

EB-01. ^{1}H-NMR (400MHz, DMSO-d6): δ 8.17 (s, 1H), 7.90 (s, 1H), 7.77 (t, 2H), 7.70-7.58 (m, 4H), 7.51 (d, 2H), 7.48 (t, 2H), 7.39-7.28 (m, 7H), 7.20-7.13 (m, 4H), 7.10 (s, 1H), 7.06 (s, 1H), 2.85-2.77 (m, 4H), 2.74 (t, J = 7.7 Hz, 2H), 1.69-1.51 (m, 6H), 1.36 (s, 12H), 1.38-1.25(m, 18H), 0.90-0.79 (m, 9H).and m/z EIMS 1094.

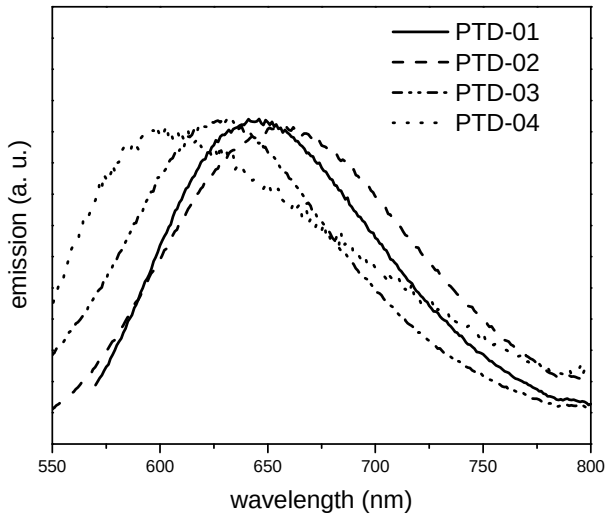


Figure S1. Emission spectra of obtained dyes in tetrahydrofuran solution.

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