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Supporting information

Highly efficient *iso*-quinoline cationic organic dyes without vinyl group for Dye-sensitized solar cells

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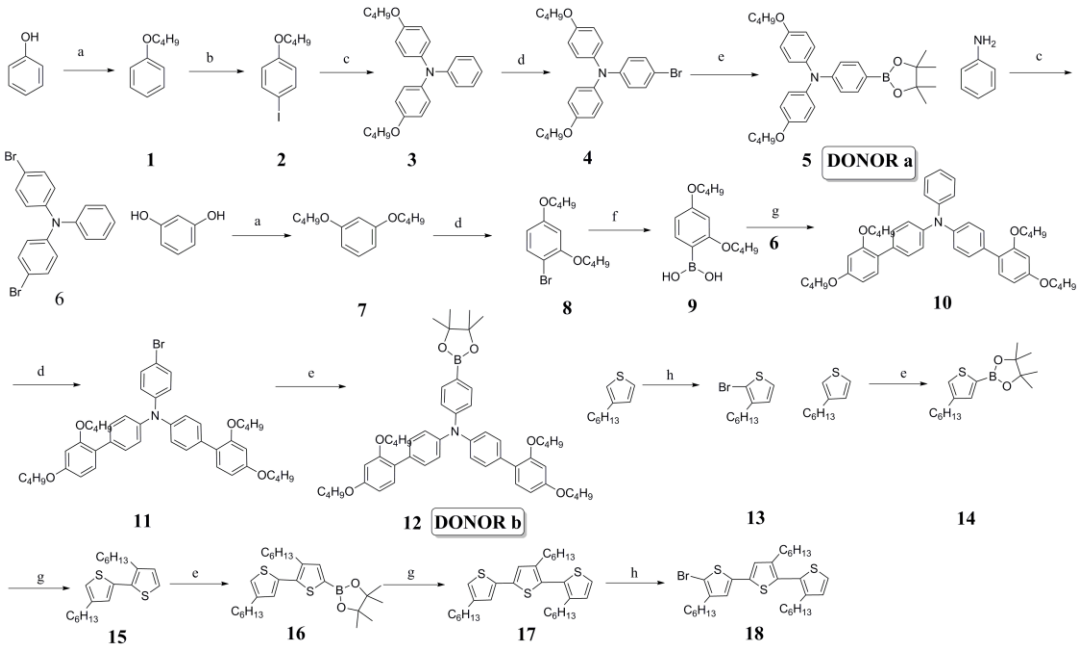
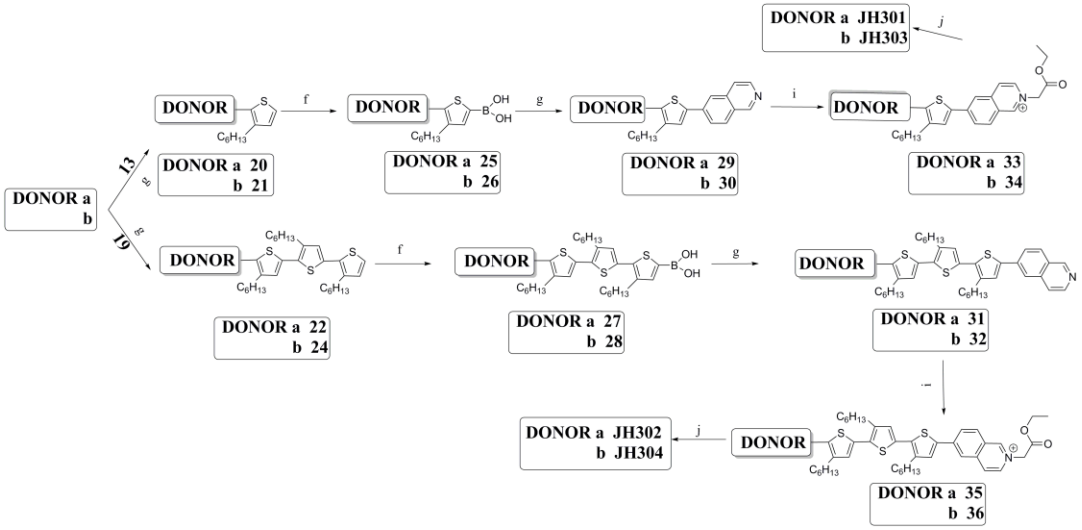
General synthetic routes



Scheme 1 Synthetic routes of the electron donors and π-conjugated moieties



Scheme 2 Synthetic routes of the sensitizers **JH301** – **JH304**

(a) 1–bromobutane, KOH, EtOH, reflux, 5 h; (b) KI, CH_3OH, H_2SO_4, H_2O_2, 60 °C, overnight; 2 h; (c) aniline, 1,10–phenanthroline, CuI, KOH, toluene, reflux, 24 h; (d) NBS, CCl_4, room temperature, 3 h; (e) *n*-BuLi, THF, – 78 °C, pinacolato boronate, 2 h; (f) *n*-BuLi, THF, – 78 °C, $B(OCH_3)_3$, 2 h; (g) K_2CO_3, $Pd(pph_3)_4$, THF/H_2O, reflux, 12 h; (h) NBS, THF, 0 °C, 3 h; (i) $BrCH_2COOEt$, acetonitrile, reflux, 12 h; (j) $LiOH{\cdot}H_2O$, EtOH /H_2O, room temperature, 24 h.

General procedure for the preparation of pinacolato boronate and boric acid (5, 9, 12, 15, 17, 25, 26, 27, 28) for Suzuki coupling

To a solution of thiophene or halogenated compound (1 equivalent) in dry THF under N_2, 2.5 M *n*-BuLi (1.2 equivalent) was dropwised at －78 ℃, the resulting mixture was stirred for 2 h at －78 ℃. Then isopropyl

pinacolato boronate (1.2 equivalent) or trimethyl borate was added. The mixture was warmed to room temperature naturally and kept for 12 h. The reaction was poured into water and extracted by CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography and dried in vacuum.

General procedure of the Suzuki reaction

Halogenated compound (1 equivalent), pinacolato boronate or boracic acid (1.2 equivalent), K_2CO_3 (1.5 equivalent), $Pd(PPh_3)_4$ (10 mg/mmol) were dissolved in THF/H_2O (5 : 1, v/v) under N_2. The mixture was refluxed for 12 h. then the reaction was cooled to the room temperature, water was added and extracted by CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography and dried in vacuum.

General procedure of the bromination

Reactants (1 equivalent) was dissolved in THF or CCl_4 at 0 ^oC, NBS (1.02 equivalent) was added for several times. The mixture was stirred for 3 h and then poured into water ,extracted by CH_2Cl_2, the organic layer was collected and concentrate by rotary evaporation. Crude product was purified by silica gel column chromatography and dried in vacuum.

General procedure of the Ullmann reaction

Aromatic amine (1 equivalent), Halogenated compound (2.5 equivalent), CuI (10%), 1, 10-phenanthroline(10%), KOH(3 equivalent) were dissolved in toluene under N_2. Then the mixture was refluxed for 24 h. After cooling to room temperature, water was added and the solution was extracted with CH_2Cl_2. the organic phase was dried with anhydrous $MgSO_4$. After removing the solvent, the residual was purified by silica gel column chromatograph.

Butoxybenzene (1) phenol (15 g, 159.5 mmol) KOH (8.95g, 233 mmol) and bromobutane (43.7 g, 319 mmol) were dissolved in EtOH solution, the mixture were refluxed for 5 h. when the reaction was finished, water was added and extracted by CH_2Cl_2. The concentrate product was purified by silica gel column chromatography and petroleum ether to give Compound **1**(20.83 g, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 6.89 (t, J = 7.8 Hz, 3H), 3.95 (t, J = 6.5 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.52 – 1.40 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). $[M]^+$ calcd. For $C_{10}H_{14}NO$, 150.1045; found, 150.1043.

1-iodo-4-butoxybenzene (2) Coupound **1** (20 g, 133 mmol) and KI (22 g, 133 mmol) were dissolved in the CH_3OH solution containing H_2SO_4 (14.2 ml, 266 mmol) in the room temperature. Then 30% H_2O_2 (30 g, 266 mmol) was added slowly and then the mixture was refluxed for 12 h. After the reaction was completed, the mixture was cooled to room temperature and 2 M Sodium thiosulfate solution was added. After extraction with CH_2Cl_2 and dried by anhydrous $MgSO_4$. The solvent was evaporated and the crude product was purified by silica gel column chromatography and ethyl acetate/petroleum ether (1 : 20, v/v) to give compound 2 (29 g, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 6.76 (dd, J = 8.7, 2H), 3.94 (td, 1.7 Hz, 2H), 1.76 – 1.67 (m, 2H), 1.52 – 1.41 (m, 2H), 0.95 (t, 3H). $[M]^+$ calcd. For $C_{10}H1_{13}OI$, 276.0011; found, 276.0022.

4-butoxy-N-(4-butoxyphenyl)-N-phenylaniline (3) Compound **3** was synthesized according to general procedure of Ullmann reaction, as colorless oil in 63% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.07 (m, 2H), 7.06 – 6.96 (m, 5H), 6.90 (dd, J = 15.4, 5.8 Hz, 2H), 6.87 – 6.73 (m, 4H), 3.91 (dt, J = 12.9, 6.3 Hz, 4H), 1.80 – 1.65 (m, 4H), 1.55 – 1.41 (m, 4H), 0.96 (t, J = 7.4 Hz, 6H). $[M]^+$ calcd. For $C_{26}H_{31}NO_2$, 389.2355; found, 389.2355.

N-(4-bromophenyl)-2-butoxy-N-(4-butoxyphenyl) aniline (4) Compound 4 was synthesized according to general procedure of bromination, as faint yellow oil in 89% yield. 1H NMR (400 MHz, CDCl3) δ 7.20 (t, J = 11.2

Hz, 2H), 6.98 (t, J = 8.7 Hz, 4H), 6.89 (d, J = 7.6 Hz, 2H), 6.79 (d, J = 8.5 Hz, 4H), 3.92 (s, 4H), 1.83 – 1.69 (m, 4H), 1.59 – 1.41 (m, 4H). 0.96 (t, J = 7.4 Hz, 6H).

4-butoxy-N-(4-butoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (5) Compound **5** was synthesized according general pinacolato boronate procedure, as faint colorless oil in 72% yield. $[M]^+$ calcd. For $C_{32}H_{42}NO_4B$, 515.3207; found, 515.3213.

4-bromo-N-(4-bromophenyl)-N-phenylaniline (6) Compound **6** was synthesized according general procedure of Ullmann reaction, as colorless solid in 71% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 4H), 7.33 (t, J = 7.9 Hz, 2H), 7.15 – 7.10 (m, 1H), 7.11 – 7.05 (m, 2H), 7.01 – 6.94 (m, 4H). $[M]^+$ calcd. For $C_{26}H_{30}B_rNO_4$, 467.1460; found, 467.1451.

1,3-dibutoxybenzene (7) Resorcinol (10 g, 90.9 mmol) KOH (7.7 g, 136.4 mmol) and bromobutane (49.8 g, 364 mmol) were dissolved in EtOH solution, the mixture were refluxed for 5 h. After the reaction was finished, water was added and extracted by CH_2Cl_2. The concentrate product was purified by silica gel column chromatography and petroleum ether to give Compound **7**(13 g, 65%). ^1H NMR (400 MHz, CDCl3) δ 7.17 – 7.11 (m, 1H), 6.48 (d, J = 2.0 Hz, 1H), 6.46 (d, J = 1.4 Hz, 2H), 3.95 – 3.89 (m, 4H), 1.74 (tt, J = 7.7, 3.8 Hz, 4H), 1.55 – 1.42 (m, 4H), 0.97 (td, J = 7.4, 1.6 Hz, 6H). $[M]^+$ calcd. For $C_{14}H_{22}O_2$, 222.1620; found, 222.1624.

1-bromo-3,5-dibutoxybenzene (8) Compound **8** was synthesized according to general procedure of bromination, as faint yellow oil in 82% yield . ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.7 Hz, 1H), 6.46 (d, J = 2.6 Hz, 1H), 6.35 (dd, J = 8.7, 2.7 Hz, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 1.85 – 1.67 (m, 4H), 1.57 – 1.41 (m, 4H), 0.97 (td, J = 7.4, 4.2 Hz, 6H). $[M]^+$ calcd. For $C_{14}H_{21}O_2Br$, 300.0725; found, 300.0729.

(3,5-dibutoxyphenyl)boronic acid (9) Compound **9** was synthesized according to general boric acid procedure, as white solid in 74% yield . $[M]^+$ calcd. For $C_{14}H_{23}O_4B$, 266.1689; found, 266.1700. $[M]^+$ calcd. For $C_{14}H_{23}O_4B$, 266.1689; found, 266.1700.

2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-N-phenyl-[1,1'-biphenyl]-4-amine (10) Compound **10** was synthesized according to general procedure of the Ullmann reaction, as colorless oil in 79% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 4H), 7.23 (dd, J = 12.8, 6.7 Hz, 4H), 7.21 – 7.16 (m, 2H), 7.13 (d, J = 8.3 Hz, 4H), 6.98 (dd, J = 10.7, 3.7 Hz, 1H), 6.53 (d, J = 9.0 Hz, 4H), 5.98 (s, 2H), 3.96 (dt, J = 10.6, 6.4 Hz, 8H), 1.80 – 1.70 (m, 8H), 1.47 (ddd, J = 29.5, 14.9, 7.4 Hz, 8H), 0.95 (dt, J = 23.4, 7.4 Hz, 12H). $[M]^+$ calcd. For $C_{46}H_{55}NO_4$, 685.43130; found, 685.4130.

N-(4-bromophenyl)-2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-[1,1'-biphenyl]-4-amine (11) Compound **11** was synthesized according to general procedure of bromination, as colorless oil in 65% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 4H), 7.27 (dd, J = 12.8, 6.7 Hz, 4H), 7.24 – 7.20 (m, 2H), 7.15 (d, J = 8.3 Hz, 4H), 6.58 (d, J = 9.0 Hz, 4H), 3.99 (dt, J = 10.6, 6.4 Hz, 8H), 1.82 – 1.71 (m, 8H), 1.49 (ddd, J = 29.5, 14.9, 7.4 Hz, 8H), 0.98 (dt, J = 23.4, 7.4 Hz, 12H). $[M]^+$ calcd. For $C_{46}H_{54}NO_4Br$, 763.3236; found, 763.3246.

2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)-[1,1'-biphenyl]-4-amine (12) Compound **12** was synthesized according to general procedure of pinacolato boronate, as white oil in 48% yield. $[M]^+$ calcd. For $C_{52}H_{66}NO_6B$, 811.4983; found, 811.5038.

2-bromo-3-hexylthiophene (13) Compound **13** was synthesized according to general procedure of bromination, as white oil in 98% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, 1H), 6.80 (d, 1H), 2.57 (t, 2H), 1.60-1.53 (m, 2H), 1.38-1.28 (m, 6H), 0.91 (t, 3H). $[M]^+$ calcd. For $C_{10}H_{16}S$, 246.0078; found, 246.0076.

2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14) Compound **14** was synthesized according to general procedure of pinacolato boronate, as white oil in 85% yield. $[M]^+$ calcd. For $C_{16}H_{27}BO_2S$, 294.1825; found, 294.1828.

3,4'-dihexyl-2,2'-bithiophene (15) Compound **15** was synthesized according to general procedure of Suzuki reaction, as white oil in 92% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, 1H), 7.03 (s, 1H), 6.89-6.92 (m, 2H),

2.74 (t, 4H), 1.52-1.70 (m, 4H), 1.20-1.35 (m, 12H), 0.84-0.92 (m, 6H). $[M]^+$ calcd. For $C_{20}H_{30}S$, 334.1789; found, 334.1782.

2-(3,4'-dihexyl-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16) Compound **16** was synthesized according to general procedure of pinacolato boronate, as yellow oil in 74% yield. $[M]^+$ calcd. For $C_{26}H_{41}BO_2S_2$, 460.2641; found, 460.2634.

3,3',4''-trihexyl-2,2':5',2''-terthiophene (17) Compound **17** was synthesized according to general procedure of Suzuki reaction, as yellow oil in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, 1H), 6.97 (d,1H), 6.93 (s, 1H), 6.93 (d, 1H), 6.90 (d, 1H), 2.75 (t, 6H), 1.74-1.55 (m, 6H), 1.37-1.26 (m,18H), 0.89-0.84 (t, 9H). $[M]^+$ calcd. For $C_{30}H_{44}S_3$, 500.2605; found, 500.2613.

5''-bromo-3,3',4''-trihexyl-2,2':5',2''-terthiophene (18) Compound **18** was synthesized according to general procedure of bromination, as yellow oil in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 1H), 6.93 (s, 1H), 6.90 (d, 1H), 6.86 (s, 1H), 2.73 (t, 6H), 1.67–1.57 (m, 6H), 1.35 – 1.25 (m, 18H), 0.94–0.85 (m, 9H); $[M]^+$ calcd. For $C_{30}H_{43}BrS_3$, 578.1710; found, 578.1703).

4-butoxy-N-(4-butoxyphenyl)-N-(4-(3-hexylthiophen-2-yl)phenyl)aniline (19) Compound **19** was synthesized according to general procedure of Suzuki reaction, as yellow oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 10.6 Hz, 2H), 7.08 (d, J = 14.9 Hz, 4H), 7.04 – 6.96 (m, 3H), 6.84 (d, J = 8.6 Hz, 4H), 3.97 – 3.88 (m, 4H), 2.72 – 2.52 (m, 2H), 1.76 – 1.67 (m, 4H), 1.58 (m, 2H), 1.53 – 1.41 (m, 4H), 1.27 (dd, J = 17.8, 5.2 Hz, 6H), 0.95 (t, J = 7.4 Hz, 6H), 0.86 – 0.79 (m, 3H). $[M]^+$ calcd. For $C_{36}H_{45}NO_2S$, 555.3171; found, 555.3162.

2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-N-(4-(3-hexylthiophen-2-yl)phenyl)-[1,1'-biphenyl]-4-amine (20) Compound **20** was synthesized according to general procedure of Suzuki reaction, as yellow oil in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 8.3 Hz, 4H), 7.27 (dd, J = 12.8, 6.7 Hz, 4H), 7.22 – 7.18 (m, 2H), 7.15 (d, J = 8.3 Hz, 4H), 7.04 (d, J = 8.3 Hz, 1H), 6.58 (d, J = 9.0 Hz, 4H), 3.98 (dt, J = 10.6, 6.4 Hz, 8H), 2.66 (t, 2H), 2.14 (s, 2H), 1.82 – 1.72 (m, 8H), 1.58 (m, 2H), 1.47 (ddd, J = 29.5, 14.9, 7.4 Hz, 8H), 1.27 (dd, J = 17.8, 5.2 Hz, 6H), 0.98 (dt, J = 23.4, 7.4 Hz, 12H), 0.88 – 0.80 (t, 3H). $[M]^+$ calcd. For $C_{56}H_{69}NO_4S$, 851.4947; found, 851.4874.

4-butoxy-N-(4-butoxyphenyl)-N-(4-(3',3'',4-trihexyl-[2,2':5',2''-terthiophen]-5-yl)phenyl)aniline (21) Compound **21** was synthesized according to general procedure of Suzuki reaction, as yellow oil in 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 5.7 Hz, 2H), 7.22 (t, *J* = 5.2 Hz, 1H), 7.07 (t, *J* = 10.1 Hz, 2H), 6.98 (d, *J* = 5.5 Hz, 4H), 6.92 (m, 3H), 6.87 – 6.80 (m, 4H), 3.93 (t, 5H), 2.81 – 2.74 (m, 6H), 1.75 (dd, *J* = 13.8, 6.4 Hz, 4H), 1.64 (m, 6H), 1.29 (m, 22H), 0.98 –0.89 (t, *J* = 7.3 Hz, 15H). $[M]^+$ calcd. For $C_{56}H_{73}NO_2S_3$,887.4803; found, 887.4785.

2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-N-(4-(3',3'',4-trihexyl-[2,2':5',2''-terthiophen]-5-yl)phenyl)-[1,1'-biphenyl]-4-amine (22) Compound **22** was synthesized according to general procedure of Suzuki reaction, as yellow oil in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 8.3 Hz, 4H), 7.27 (dd, J = 12.8, 6.7 Hz, 4H), 7.21 – 7.16 (m, 2H), 7.12 (d, J = 8.3 Hz, 4H), 7.04 (d, J = 8.3 Hz, 1H), 6.93 (s, 2H), 6.53 (d, J = 9.0 Hz, 4H), 3.96 (dt, J = 10.6, 6.4 Hz, 8H), 2.72 (t, J = 10.6, 6.4 Hz, 6H), 1.80 – 1.70 (m, 8H), 1.57 – 1.26 (m, 34H), 0.95 (m, 21H). $[M]^+$ calcd. For $C_{76}H_{97}NO_4S_3$,1183.658; found,1183.6482.

(5-(4-(bis(4-butoxyphenyl)amino)phenyl)-4-hexylthiophen-2-yl)boronicacid (23) Compound **23** was synthesized according to general procedure of boric acid, as yellow oil in 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 10.6 Hz, 2H), 7.11 (d, J = 14.9 Hz, 4H), 7.07 – 6.99 (d, J = 10.6 Hz, 2H), 6.89 (d, J = 14.9 Hz, 4H), 3.97 – 3.88 (m, 4H), 2.75 – 2.55 (m, 2H), 2.28 (s, 2H), 1.74 – 1.65 (m, 4H), 1.60 (m, 2H), 1.53 – 1.41 (m, 4H), 1.30 (dd, J = 17.8, 5.2 Hz, 6H), 0.95 (t, J = 7.4 Hz, 6H), 0.86 – 0.79 (m, 3H).

(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-4-hexylthiophen-2-yl)boronic acid (24) Compound **24** was synthesized according to general procedure of boric acid, as yellow oil in 58% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 4H), 7.23 (dd, J = 12.8, 6.7 Hz, 4H), 7.21 – 7.16 (m, 2H), 7.13 (d, J = 8.3 Hz, 4H), 7.02 (s, 1H), 6.53 (d, J = 9.0 Hz, 4H), 3.96 (dt, J = 10.6, 6.4 Hz, 8H), 2.62 (t, 2H), 2.14 (s, 2H), 1.80 – 1.70 (m, 8H), 1.58 (m, 2H), 1.47 (ddd, J = 29.5, 14.9, 7.4 Hz, 8H), 1.27 (dd, J = 17.8, 5.2 Hz, 6H), 0.95 (dt, J = 23.4, 7.4 Hz, 12H), 0.86 – 0.79 (t, 3H).

(5''-(4-(bis(4-butoxyphenyl)amino)phenyl)-3,4',4''-trihexyl-[2,2':5',2''-terthiophen]-5-yl)boronic acid (25) Compound **25** was synthesized according to general procedure of boric acid, as yellow oil in 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 11.4 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 4.9 Hz, 4H), 6.98 (m, 3H), 6.85 (d, *J* = 8.6 Hz, 4H), 3.97 (m, 8H), 2.81 (d, *J* = 7.0 Hz, 6H), 1.84 – 1.73 (m, 4H), 1.58 – 1.48 (m, 6H), 1.32 (s, 22H), 1.00 – 0.92 (t, *J* = 12.4 Hz, 15H).

(5''-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-3,4',4''-trihexyl-[2,2':5',2''-terthiophen]-5-yl)boronic acid (26) Compound **26** was synthesized according to general procedure of boric acid, as yellow oil in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.3 Hz, 4H), 7.25 (dd, J = 12.8, 6.7 Hz, 4H), 7.22 – 7.18 (m, 2H), 7.13 (d, J = 8.3 Hz, 4H), 7.04 (d, J = 8.3 Hz, 1H), 6.95 (s, 2H), 6.53 (d, J = 9.0 Hz, 4H), 3.96 (dt, J = 10.6, 6.4 Hz, 8H), 2.32 (t, J = 10.6, 6.4 Hz, 6H), 2.18 (s, 2H), 1.80 – 1.70 (m, 8H), 1.57 – 1.26 (m, 34H), 0.95 (m, 21H).

4-butoxy-N-(4-butoxyphenyl)-N-(4-(3-hexyl-5-(isoquinolin-6-yl)thiophen-2-yl)phenyl)aniline (27) Compound **27** was synthesized according to general procedure of Suzuki reaction, as orange oil in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 8.02 (s, 1H), 7.56 (d, J = 5.2 Hz, 2H), 7.24 (d, J = 10.6 Hz, 2H), 7.13 (d, J = 14.9 Hz, 4H), 7.09 – 6.99 (m, 2H), 6.93 (s, 1H), 6.88 (d, J = 8.6 Hz, 4H), 3.97 – 3.88 (m, 4H), 2.62 (t, 2H), 1.76 – 1.67 (m, 4H), 1.58 (m, 2H), 1.53 – 1.41 (m, 4H), 1.27 (dd, J = 17.8, 5.2 Hz, 6H), 0.95 (t, J = 7.4 Hz, 6H), 0.86 – 0.79 (m, 3H). $[M]^+$ calcd. For $C_{45}H_{50}N_2O_2S$, 682.3593; found,682.3622.

2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-N-(4-(3-hexyl-5-(isoquinolin-6-yl)thiophen-2-yl)phenyl)-[1,1'-biphenyl]-4-amine (28) Compound **28** was synthesized according to general procedure of Suzuki reaction, as orange oil in 75 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.35 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 8.05 (s, 1H), 7.58 (d, J = 5.2 Hz, 2H), 7.47 (d, J = 8.3 Hz, 4H), 7.25 (dd, J = 12.8, 6.7 Hz, 4H), 7.21 – 7.16 (m, 2H), 7.13 (d, J = 8.3 Hz, 4H), 7.02 (s, 1H), 6.53 (d, J = 9.0 Hz, 4H), 3.96 (dt, J = 10.6, 6.4 Hz, 8H), 2.62 (t, 2H), 2.14 (s, 2H), 1.80 – 1.70 (m, 8H), 1.58 (m, 2H), 1.47 (ddd, J = 29.5, 14.9, 7.4 Hz, 8H), 1.27 (dd, J = 17.8, 5.2 Hz, 6H), 0.95 (dt, J = 23.4, 7.4 Hz, 12H), 0.86 – 0.79 (t, 3H). $[M]^+$ calcd. For $C_{65}H_{74}N_2O_2S_3$, 978.5369; found, 978.5437.

4-butoxy-N-(4-butoxyphenyl)-N-(4-(3',3'',4-trihexyl-5''-(isoquinolin-6-yl)-[2,2':5',2''-terthiophen]-5-yl)phenyl)aniline (29) Compound **29** was synthesized according to general procedure of Suzuki reaction, as orange oil in 83 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 28.1 Hz, 1H), 8.48 (d, *J* = 25.8 Hz, 1H), 8.04 (s, 1H), 7.84 – 7.63 (d, *J* = 16.7 Hz, 3H), 7.40 – 7.32 (d, 2H), 7.28 (m, 2H), 7.10 (d, *J* = 6.8 Hz, 4H), 6.94 (d, *J* = 6.8 Hz, 3H), 6.85 (d, *J* = 6.9 Hz, 4H), 3.99(t, 8H), 2.83 (s, 6H), 1.74 (m, 4H), 1.65 (m, 6H), 1.35 – 1.23 (m, 22H), 0.97 (t, 15H), 0.90 (s, 35H). $[M]^+$ calcd. For $C_{65}H_{78}N_2O_4S$,1014.5225; found,1014.5615.

2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-N-(4-(3',3'',4-trihexyl-5''-(isoquinolin-6-yl)-[2,2':5',2''-terthiophen]-5-yl)phenyl)-[1,1'-biphenyl]-4-amine (30) Compound **29** was synthesized according to general procedure of Suzuki reaction, as orange oil in 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.35 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.02 (s, 1H), 7.56 (d, J = 5.2 Hz, 2H), 7.44 (d, J = 8.3 Hz, 4H), 7.25 (dd, J = 12.8, 6.7 Hz, 4H), 7.20 – 7.15 (m, 2H), 7.10 (d, J = 8.3 Hz, 4H), 7.01 (d, J = 8.3 Hz, 1H), 6.93 (s, 2H), 6.55 (d, J = 9.0 Hz, 4H), 3.98 (dt, J = 10.6, 6.4 Hz, 8H), 2.36 (t, J = 10.6, 6.4 Hz, 6H), 1.80 – 1.70 (m, 8H), 1.57 – 1.26 (m, 34H), 0.95 (m, 21H). $[M]^+$ calcd. For $C_{85}H_{102}N_2O_4S_3$, 1310.7002; found,1310.6113.

6-(5-(4-(bis(4-butoxyphenyl)amino)phenyl)-4-hexylthiophen-2-yl)-2-(2-ethoxy-2-oxoethyl)isoquinolin-2-ium (31) Compound **30** (150 mg, 0.22 mmol) and $BrCH_2COOEt$ (0.24 ml, 2.2 mmol) was dissolved in 10 ml CH_3CN, the mixture was refluxed for 12 h. when the reaction was finished, the mixture was concentrated by rotary evaporation. The crude red solid was purified by silica gel column chromatograph with CH_2Cl_2/ CH_3OH (12 : 1, v/v) to give compound 31 (138 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.65 (d, J = 8.2 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.10 (s, 1H), 7.62 (d, J = 5.2 Hz, 2H), 7.37 (d, J = 10.6 Hz, 2H), 7.08 (d, J = 14.9 Hz, 4H), 7.04 – 6.98 (m, 2H), 6.94 (s, 3H), 6.86 (d, J = 8.6 Hz, 4H), 6.22 (s, 2H), 4.33 – 4.28 (m, 2H), 3.73 (q, J = 7.0 Hz, 2H), 2.87 – 2.72 (m, 6H), 2.65 (s, 3H), 1.48 (dd, J = 14.8, 7.5 Hz, 6H), 1.30 (m, J = 17.7, 10.4, 4.8 Hz, 25H), 0.98 (d, J = 7.4 Hz, 6H), 0.89 (dd, J = 10.5, 5.7 Hz, 9H). $[M]^+$ calcd. For $C_{49}H_{57}N_2O_4S$,769.4039; found, 769.2312.

6-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-4-hexylthiophen-2-yl)-2-(2-ethoxy-2-oxoethyl)isoquinolin-2-ium (32) The synthesis procedure was similar to procedure of systhesis Compound **31**. A red solid was obtaind in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.75 (d, J = 8.2 Hz, 1H), 8.45 (d, J = 8.2 Hz, 1H), 8.00 (d, 2H), 7.52 (d, J = 5.2 Hz, 2H), 7.46 (d, J = 8.3 Hz, 4H), 7.28 (dd, J = 12.8, 6.7 Hz, 4H), 7.22 – 7.18 (m, 2H), 7.12 (d, J = 8.3 Hz, 4H), 7.04 (s, 1H), 6.57 (d, J = 9.0 Hz, 4H), 5.98 (s, 2H), 3.99 (m, 10H), 2.62 (t, 2H), 1.80 – 1.70 (m, 8H), 1.58 – 1.47 (ddd, J = 29.5, 14.9, 7.4 Hz, 10H), 1.27 (m, 9H), 0.95 – 0.85 (dt, J = 23.4, 7.4 Hz, 15H). $[M]^+$ calcd. For $C_{69}H_{81}N_2O_6S$, 1065.5815; found, 1065.5802.

6-(5''-(4-(bis(4-butoxyphenyl)amino)phenyl)-3,4',4''-trihexyl-[2,2':5',2''-terthiophen]-5-yl)-2-(2-ethoxy-2-oxoethyl)isoquinolin-2-ium (33) The synthesis procedure was similar to procedure of synthesis Compound **31**. A red solid was obtaind in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.65 (d, J = 8.2 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.10 (s, 1H), 7.62 (d, J = 5.2 Hz, 2H), 7.37 (d, J = 10.6 Hz, 2H), 7.08 (d, J = 14.9 Hz, 4H), 7.04 – 6.98 (m, 2H), 6.94 (s, 3H), 6.86 (d, J = 8.6 Hz, 4H), 6.22 (s, 2H), 4.33 – 4.28 (s, 2H), 3.73 (t, 4H), 2.87 – 2.72 (m, 6H),1.72-1.65(m, 4H) 1.48 (dd, J = 14.8, 7.5 Hz, 6H), 1.30 (m, J = 17.7, 10.4, 4.8 Hz, 25H), 0.98 (d, J = 7.4 Hz, 6H), 0.89 (dd, J = 10.5, 5.7 Hz, 9H). $[M]^+$ calcd. For $C_{69}H_{85}N_2O_4S_3$, 1101.5672; found, 1101.5713.

6-(5''-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-3,4',4''-trihexyl-[2,2':5',2''-terthiophen]-5-yl)-2-(2-ethoxy-2-oxoethyl)isoquinolin-2-ium (34) The synthesis procedure was similar to procedure of synthesis Compound **31**. A red solid was obtaind in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.75 (d, J = 8.2 Hz, 1H), 8.45 (d, J = 8.2 Hz, 1H), 8.00 (s, 1H), 7.52 (d, J = 5.2 Hz, 2H), 7.42 (d, J = 8.3 Hz, 4H), 7.23 (dd, J = 12.8, 6.7 Hz, 4H), 7.21 – 7.16 (m, 2H), 7.13 (d, J = 8.3 Hz, 4H), 7.02 (s, 1H), 6.92 (s, 2H), 6.53 (d, J = 9.0 Hz, 4H), 5.97 (s, 2H), 3.96 (m, 10H), 2.62 (t, 6H), 1.80 – 1.70 (m, 8H), 1.58 (m, 6H), 1.47 (ddd, J = 29.5, 14.9, 7.4 Hz, 8H), 1.27 (m, 21H), 0.95–0.79 (t, 21H). $[M]^+$ calcd. For $C_{89}H_{109}N_2O_6S_3$, 1397.7448; found, 1397.7496.

6-(5-(4-(bis(4-butoxyphenyl)amino)phenyl)-4-hexylthiophen-2-yl)-2-(carboxymethyl)isoquinolin-2-ium (JH301) Compound **31**(76 mg, 0.10 mmol) and $LiOH{\cdot}H_2O$(42 mg, 1 mmol) were dissolved in EtOH. The mixture was stirred at room temperature for 24 h. 2 M HCl was added to adjust PH to neurtrality. Then the mixture was extracted by CH_2Cl_2 and evaporated to dryness. The crude red solid was purified by silica gel column chromatograph with CH_2Cl_2/ CH_3OH (5 : 1, v/v) to give a red solid (28 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, J = 101.4 Hz, 1H), 8.35 (d, J = 81.9 Hz, 2H), 7.85 (d, J = 79.9 Hz, 2H), 7.37 (d, J = 57.9 Hz, 2H), 7.08 (d, J = 35.4 Hz, 7H), 6.85 (d, J = 70.1 Hz, 6H), 5.46 (s, 2H), 3.89 (s, 6H), 2.32 (d, J = 59.1 Hz, 2H),1.80 – 1.68 (m, 4H), 1.54 – 1.45 (ddd, J = 29.5, 14.9, 7.4 Hz, 6H), 1.31– 1.27 (m, 4H), 0.95 – 0.85 (dt, J = 23.4, 7.4 Hz, 9H). $[M]^+$ calcd. For $C_{47}H_{53}N_2O_4S$, 741.3726; found, 741.2327.

6-(5''-(4-(bis(4-butoxyphenyl)amino)phenyl)-3,4',4''-trihexyl-[2,2':5',2''-terthiophen]-5-yl)-2-(carboxymethyl)isoquinolin-2-ium (**JH302**) The synthesis procedure was similar to the synthesis procedure of **JH301**. A red solid was obtained in 33%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.49 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.99 (s, 1H), 7.68 (d, J = 5.2 Hz, 2H), 7.48 (d, J = 10.6 Hz, 2H), 7.19 (d, J = 14.9 Hz, 4H), 7.04 – 6.98 (m, 2H), 7.01 (s, 3H), 6.77 (d, J = 8.6 Hz, 4H), 6.44 (s, 2H), 3.73 (t, J = 7.0 Hz, 4H), 2.65 (t, 6H), 1.73-1.59 (m, 4H),

1.48 (dd, J = 14.8, 7.5 Hz, 6H), 1.3–1.25 (m, J = 17.7, 10.4, 4.8 Hz, 22H), 1.04 (d, J = 7.4 Hz, 6H), 0.88 (dd, J = 10.5, 5.7 Hz, 9H). $[M]^+$ calcd. For $C_{67}H_{81}N_2O_4S_3$, 1073.5358; found, 1073.4.

6-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-4-hexylthiophen-2-yl)-2-(carboxymethyl)isoquinolin-2-ium (JH303) The synthesis procedure was similar to procedure of systhesis of **JH301**. A red solid was obtaind in 27% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.59 (d, 1H), 7.94 (d, 1H), 7.87 (d, 2H), 7.53 (d, 2H), 7.15 (d, 4H), 7.11 (d, 4H), 6.97 (m, 2H), 6.95 (d, 4H), 6.85(s, 1H), 6.77 (d, 4H), 5.98 (s, 2H), 3.99 (m, 8H), 2.62 (t, 2H), 1.80 – 1.70 (m, 8H), 1.58 – 1.44 (m, 10 H), 1.3 – 1.24 (m, 6H), 0.95-0.88 (t, 15H). $[M]^+$ calcd. For $C_{69}H_{85}N_2O_4S_3$, 1037.5502; found, 1037.2509.

6-(5''-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-3,4',4''-trihexyl-[2,2':5',2''-terthiophen]-5-yl)-2-(carboxymethyl)isoquinolin-2-ium (JH304) The synthesis procedure was similar to the synthesis procedure of **JH301.** A red solid was obtained in 23%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.70 (d, J = 8.2 Hz, 1H), 8.42 (d, J = 8.2 Hz, 1H), 7.93 (s, 1H), 7.68 (d, J = 5.2 Hz, 2H), 7.56 (d, J = 8.3 Hz, 4H), 7.37 (dd, J = 12.8, 6.7 Hz, 4H), 7.23 – 7.19(m, 2H), 7.13 (d, J = 8.3 Hz, 4H), 6.93 (s, 1H), 6.90 (s, 2H), 6.47 (d, J = 9.0 Hz, 4H), 5.97 (s, 2H), 3.92 (m, 8H), 2.62 (t, 6H), 1.80 – 1.70 (m, 8H), 1.58 (m, 6H), 1.47 (ddd, J = 29.5, 14.9, 7.4 Hz, 8H), 1.27 (m, 18H), 0.95–0.79 (t, 21H). $[M]^+$ calcd. For $C_{87}H_{105}N_2O_6S_3$, 1369.7135; found, 1369.6.

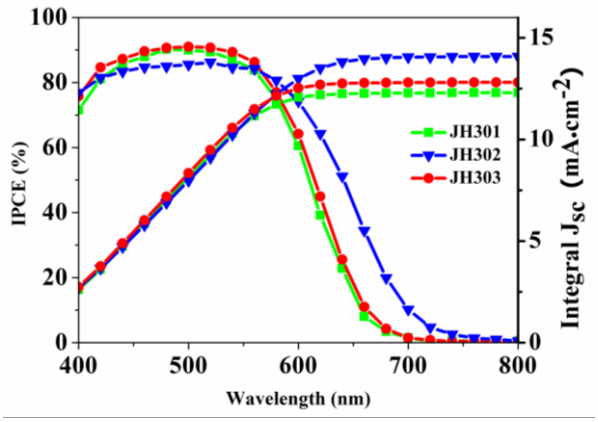


Fig. 5b IPCE and integral current density of the DSSSCs sensitized by **JH** series of dyes