Supporting information

Synthesis of Multi-donor Dyes and Influence of Molecular Design on Dye-sensitized Solar Cells

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Synthesis of 4-bromo-N,N-dihexylaniline (6)

4-Bromoaniline (5 g, 29 mmol) and 1-bromohexane (10.2 mL, 73 mmol) were heated to 130 °C and stirred for 18 hours. The reaction mixture was cooled to room temperature and 2M NaOH (50 mL) was added. The aqueous layer was extracted with diethyl ether (2 x 100 mL), the combined organic layers were dried with anhydrous Na₂SO₄ and filtered. The solvent was removed under reduced pressure to obtain a black crude product, which was purified using column chromatography on silica gel with hexane as eluent to isolate pale yellow oil (3.62 g, yield 36.7%). MS (EI) m/z = 339.3 (M⁺), 340.3 (calcd.). ¹H NMR (300 MHz, CDCl₃, ppm) δ = 7.26 – 7.29 (d, 2H), 6.51 – 6.54 (d, 2H), 3.22 – 3.27 (t, 4H,), 1.56 – 1.58 (broad, 4H), 1.34 (s, 12H), 0.94 (s, 6H). Elem. Anal. Calcd. for C1₈H₃₀BrN: C, 63.52%; H, 8.88%; Br, 23.48, N, 4.12%; found: C, 63.14%; H, 8.58%; Br, 23.70, N, 4.19%.

Synthesis of 4-dihexylamino-phenylboronic acid pinacol ester (1a)

Compound 6 (3.80 g, 11.18 mmol) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere and cooled to -78 °C in dry ice / acetone bath. n-BuLi in cyclohexane (15 mL, 30 mmol) was added drop wise and stirred at -78 °C for 1 hr. To this mixture, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5 mL, 22.8 mmol) was added slowly, stirred and gradually
warmed to room temperature. The mixture was added to ice water (50 mL, 0 °C), extracted with
diethyl ether (2 x 50 mL), dried over anhydrous Na₂SO₄ and filtered. The organic solvent was
removed under reduced pressure to obtain brown oil. The crude product was purified over silica
gel column using dichloromethane (DCM)/hexane (1:4) mixture as eluent to yield orange oil
(2.72 g, 63 %). MS (EI) m/z = 387.4 (M⁺), 387.4 (calcd.). ¹H NMR (300 MHz, CDCl₃, ppm): δ =
7.66 – 7.69 (d, 4H), 6.61 – 6.64 (d, 4H), 3.27 – 3.32 (t, 4H), 1.60 (quintet, 4H), 1.33 (s, 24H),
0.91 – 0.94 (t, 6H, –CH₃). Elem. Anal. Calcd. for C₂₄H₄₂BNO₂: C, 74.41%; H, 10.93%; N,
3.62%; found: C, 74.26%; H, 10.65%; N, 3.79%.

Synthesis of 4-pyrrolidino-1-bromobenzene (8)
1-Bromo-4-iodobenzene (5 g, 17.75 mmol), iron(III) chloride (0.29 g, 1.79 mmol), copper(II)
oxide (0.14 g, 1.76 mmol), rac-BINOL (1.02 g, 3.56 mmol) and cesium carbonate (12 g, 36.83
mmol) were taken into 250 mL round bottom flask, connected to vacuum for removing the air
and backfilled with nitrogen gas. A solution of pyrrolidine (1.75 mL, 21.32 mmol) in DMF (35
mL) was added and the reaction mixture was stirred at 90 °C for 18 hours. After cooling to room
temperature, the mixture was diluted with DCM (100 mL) and filtered to remove insoluble
solids. The insoluble residue was rinsed with DCM, filtrate was washed with 1M NaOH (200
mL) followed by water (100 mL), combined organic layer was dried over anhydrous Na₂SO₄,
filtered, concentrated under reduced pressure and the crude product was purified using column
chromatography with DCM : Hexane (1:10) mixture as eluent to get a white solid (3.41 g, yield
85%). MS (EI) m/z = 224.1 (M⁺), 226.1 (calcd.). ¹H NMR (300 MHz, CDCl₃, ppm): δ =
7.26 – 7.30 (d, 2H), 6.44 – 6.47 (d, 2H), 3.23 – 3.27 (t, 4H), 1.99 – 2.03 (quintet, 4H). ¹³C NMR (δ,
75.4 MHz, CDCl₃) ppm: δ = 146.69, 131.66, 113.27, 47.77, 25.43. Elem. Anal. Calcd. for
C₁₀H₁₂BrN: C, 53.12%; H, 5.35%; Br, 35.34, N, 6.19%; found: C, 53.24%; H, 5.33%; Br, 35.80,
N, 6.27%.

Synthesis of 4-pyrrolidino-phenylboronic acid pinacol ester (1b)
Compound 8 (3.41 g, 15.1 mmol) dissolved in anhydrous THF (80 mL) was cooled to -78 °C
under nitrogen atmosphere. To this, 2M n-BuLi in cyclohexane (16 mL, 32 mmol) was added
slowly and stirred at -78 °C for 1 hr. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.2
mL, 30.4 mmol) was added slowly to the mixture, stirred and allowed to warm up to room
temperature. The reaction mixture was added to ice water (50 mL), extracted with diethyl ether
(3 x 50 mL), combined organic extracts were dried on anhydrous Na₂SO₄, filtered and the excess
solvent was removed under reduced pressure to obtain a dark brown oil. The crude product was
dissolved in minimum amount of diethyl ether, cooled to 0 °C for crystallization of the
compound as pale pink crystals and collected by filtration (2.95 g, yield 71%). MS (EI) m/z =
273.2 (M⁺), 273.2 (calcd.). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.66 – 7.69 (d, 2H), 6.54 –
6.57 (d, 2H), 3.30 – 3.34 (t, 4H), 1.98 – 2.03 (quintet, 4H), 1.32 (s, 12H). Elem. Anal. Calcd. for
C₁₆H₂₄BNO₂: C, 70.35%; H, 8.86%; N, 5.13%; found: C, 70.47%; H, 9.01%; N, 5.21%.
Figure S1. Enlarged cyclic voltammetry scans of dyes TC1 – TC5 at a scan rate of 100 mV/s in THF solution. Potentials reported with respect to ferrocene.
Figure S2. UV-vis absorption spectra of dyes (TC1, TC2, TC4 and TC5) on TiO$_2$ coated quartz plates. The plates were immersed in 0.25 mM dye solutions in THF for 24 hours and rinsed several times using fresh THF solvent.
Figure S3. IPCE (Incident photon-to-current efficiency) curves of TC1 - TC5 dyes. The electrodes were immersed into a 0.25 mM solution of sensitizer in THF solution.
1H NMR and MS spectra of compound 1a

*** Current Data Parameters ***
NAME : f9065nmh
EXPNO : 4
PROCNO : 1

*** Acquisition Parameters ***
BF1 : 300.1300000 MHz
LOCNUC : 2H
NS : 15
C1 : 1863.43 Hz
PULPROG : zg20
SFO1 : 300.1318534 MHz
SOLVENT : CDC3
SW : 17.9519 ppm

*** Processing Parameters ***
LB : 0.30 Hz
PHC0 : 223.163 degree
PHC1 : -0.157 degree

C_{6}H_{13} - N - C_{6}H_{13}
1H NMR and MS spectra of compound 1b

*** Current Data Parameters ***
NAME  : ac180mtn
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***
INSTRUM : spect
LOCNUC : 2H
NS : 8
NUCLEUS : off
C1 : 1893.43 Hz
PULPROG : zpg80
SFQ1 : 300.1318534 MHz
SOLVENT : CDCl3
SW : 17.6519 ppm
TD : 32768
TE : 298.1 K

*** Processing Parameters ***
LB : 3.0 Hz

*** 1D NMR Plot Parameters ***
NUCLEUS : off

\[
\begin{array}{c}
\text{1H NMR and MS spectra of compound 1b} \\
\end{array}
\]
1H & 13C NMR of compound 2a
MS spectra of compound 2a
1H & 13C NMR of compound TC1

*** Current Data Parameters ***
NAME : ncb001cm
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 1H
NB : 150
NUCLEUS : off
G1 : 1655.43 Hz
PULPROG : ag90
SFO1 : 300.1318534 MHz
SOLVENT : DMF
SW : 17.9519 ppm
TD : 32768
TE : 297.1 K
*** Processing Parameters ***
LB : 0.90 Hz
SF : 300.1300018 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off
FT-IR & MALDI-TOF of compound TC1
**1H & 13C NMR of compound 2b**

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**Current Data Parameters***

**NAME**: nv01omh

**EXPNO**: 1

**PRONO**: 1

**Acquisition Parameters***

**INSTRM**: spect

**LCCNUC**: 2H

**NE**: 12

**NLCLEUS**: off

**CI**: 1863.43 Hz

**PULPROG**: zg30

**SFD1**: 300.1318534 MHz

**SOLVENT**: CDCl₃

**SW**: 17.9519 ppm

**TD**: 32768

**TE**: 297.1 K

**Processing Parameters***

**LB**: 0.30 Hz

**1D NMR Plot Parameters***

**NLCLEUS**: off

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![Chemical Structure](attachment:image.png)
The image contains a chemical structure of a compound with the following chemical formula: N-phenylpyrrole-thiophene CHO. Additionally, there are sections labeled as **Current Data Parameters**:

- **NAME**: akt1103
- **EXPNO**: 2
- **PROCNO**: 1
- **Acquisition Parameters**:
  - **BF1**: 126.767860 MHz
  - **LOCNUC**: 2H
  - **NS**: 3615
  - **O1**: 13204.57 Hz
  - **PULPROX**: 1
  - **D1**: 126.770000 MHz
  - **SOLVENT**: CDCl3
  - **SV**: 238.7615 ppm
- **Processing Parameters**:
  - **LS**: 1.00 Hz
  - **T1**: 202.644 degree
  - **PH1**: 51.363 degrees
1H & 13C NMR of compound **TC2**
FT-IR & MALDI-TOF of compound TC2
$1H \& 13C$ NMR of compound 3c
Mass spectra of compound 3c
1H & 13C NMR of compound TC3
FT-IR & MALDI-TOF of compound TC3
**1H & 13C NMR of compound 3b**

***Current Data Parameters***
- NAME: 3b
- EXPNO: 3
- PROINO: 1

***Acquisition Parameters***
- SFI: 500.1318 MHz
- LOCNUC: 2H
- NB: 8
- C1: 1853.43 Hz
- PULPROG: zg20
- SFO1: 500.1318 MHz
- SOLVENT: CDCl3
- BW: 17.9519 ppm

***Processing Parameters***
- LB: 0.30 Hz
- PHC0: 303.400 degrees
- PHC1: -0.157 degrees
*** Current Data Parameters ***
NAME : sk1024
EXPNO : 2
PROCNC : 1

*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
LOCNUC : 2H
NS : 1024
O1 : 13204.67 Hz
PULPROG : zgspgl
SFQ1 : 125.7709296 MHz
SOLVENT : CDCl3
BW : 238.7676 ppm

*** Processing Parameters ***
LB : 1.00 Hz
PHC0 : 183.918 degree
PHC1 : 21.026 degree
Mass spectra of compound 3b
1H NMR & FT-IR of compound TC4
FTIR Dye <MTH-2>
30th Oct 2012
MALDI-TOF of compound TC4
1H & 13C NMR of compound 4
Mass spectra of compound 4

Average of 4.455 to 4.806 min: TC1097 Didata ms (-)

m/z →

44.0 91.1 119.1 173.0 221.1 253.2 346.3 427.2 471.1 506.1 535.1 563.3 636.3 654.4 721.4 751.5 793.5 838.0 869.5 900.5 943.0
1H & 13C NMR of compound TC5
FT-IR and MALDI-TOF of compound TC5