Organic Dyes Incorporating Low Band Gap Chromophores for Dye-Sensitized Solar Cells

Marappan Velusamy,[†] K. R. Justin Thomas,[†] Jiann T. Lin,[†*] Ying-Chan Hsu,[‡] and Kuo-Chuan Ho[‡*]

[†]Institute of Chemistry, Academia Sinica, 115 Nankang, Taipei, Taiwan; [‡]Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

Supporting Information

Synthesis of the dyes

General. All reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. The starting materials 4,7-dibromobenzo[1,2,5]thiadiazole[1], 4,7-dibromobenzo[1,2,5]selenadiazole[2], N,N-diphenyl-4-aminophenylboronic acid[3], diphenyl-(5-tributylstannanyl-thiophen-2-yl)-amine[4] and 2-tributylstannyl-5-dioxolanyl thiophene[5] were prepared by adopting literature procedures. Other general spectroscopic instrumentation were described in an earlier report.[6]

Synthesis of the precursors 3, 4, 10, and 11. Compounds [4-(7-Bromo-benzo[1,2,5]thiadiazol-4-yl)-phenyl]-diphenyl-amine (**3)** and [4-(7-Bromo-benzo[1,2,5]selenadiazol-4-yl)-phenyl]-diphenyl-amine **(4)** were synthesized from 4,7-dibromobenzo[1,2,5]thiadiazole or 4,7-dibromobenzo[1,2,5] selenadiazole on reaction with N,N-diphenyl-4-aminophenylboronic acid under Suzuki coupling conditions. Compounds [5-(7-Bromo-benzo[1,2,5]thiadiazol-4-yl) -thiophen-2-yl]-diphenyl-amine (**10)** and [5-(7-Bromo-benzo[1,2,5]selenadiazol-4-yl) -thiophen-2-yl]-diphenyl-amine (**11)** were synthesized by Stille coupling reactions of 4,7-dibromobenzo[1,2,5]thiadiazole or

4,7-dibromobenzo[1,2,5] selenadiazole with diphenyl-(5-tributylstannanyl-thiophen-2-yl)-amine.

[4-(7-Bromo-benzo[1,2,5]thiadiazol-4-yl)-phenyl]-diphenyl-amine (3). A stirred mixture of 4,7-dibromobenzo[1,2,5]thiadiazole **1** (2.94 g, 10 mmol), N,N-diphenyl-4-aminophenylboronic acid (2.9 g, 10 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.15 mmol), Na_2CO_3 (1.47 g, 10 mmol), Toluene (10 ml), THF (10 ml) and H_2O (2 ml) was heated at reflux for 24 h. When the reaction was completed, water was added to quench the reaction. The product was extracted with diethyl ether. The organic layer was collected, dried over anhydrous $MgSO_4$ and evaporated under vacuum. The solid was adsorbed on silica gel and purified by column chromatography, using CH_2Cl_2/hexane mixture as eluent to give **3** as dark yellow solid (2.4 g, 54 %). ^{1}H NMR (δ, $CDCl_3$): 7.05 (t, *J* = 7.4 Hz, 2H), 7.15-7.18 (m, 6H), 7.25-7.29 (m, 4H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.76-7.79 (m, 2H), 7.86 (d, *J* = 7.4 Hz, 1H). FAB MS (m/z): 457.0 (M^+).

[4-(7-Bromo-benzo[1,2,5]selenadiazol-4-yl)-phenyl]-diphenyl-amine (4). Orange solid, Yield: 51 %. ^{1}H NMR (δ, $CDCl_3$): 7.03 (t, *J* = 7.4 Hz, 2H), 7.12-7.18 (m, 6H), 7.23-7.29 (m, 4H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.68-7.72 (m, 2H), 7.80 (d, *J* = 7.4 Hz, 1H). FAB MS (m/z): 505.0 (M^+).

[5-(7-Bromo-benzo[1,2,5]thiadiazol-4-yl)-thiophen-2-yl]-diphenyl-amine (10). 4,7-Dibromobenzo[1,2,5]thiadiazole **1** (2.94 g, 10 mmol) diphenyl-(5-tributylstannanyl-thiophen-2-yl)-amine (5.4 g, 10 mmol) and $Pd(PPh_3)_2Cl_2$ (140 mg) were charged in a 250 mL round-bottom flask. DMF (15 mL) was added and the contents were heated to 80 °C and maintained at this temperature for 24 h. After the reaction was complete the reaction mixture was diluted with methanol. The precipitate obtained was filtered and washed with methanol, and dried. The residue was adsorbed on silica gel and purified by column chromatography using dichloromethane/hexane mixture as eluent to give compound **10** as purple solid (2.15 g, 46%). ^{1}H NMR (δ, $CDCl_3$): 6.67 (d, *J* = 4 Hz, 1H), 7.05-7.09 (m, 2H), 7.20-7.30 (m, 8H),

7.49 (d, *J* = 7.4, 1H), 7.74 (d, *J* = 7.4, 1H), 7.95 (d, *J* = 4 Hz, 1H). FAB MS (m/z): 463.0 (M^+).

[5-(7-Bromo-benzo[1,2,5]selenadiazol-4-yl)-thiophen-2-yl]-diphenyl-amine (11). Purple solid, Yield: 34 %. ^{1}H NMR (δ, $CDCl_3$): 6.64 (d, *J* = 4 Hz, 1H), 7.00-7.02 (m, 2H), 7.12-7.25 (m, 8H), 7.39 (d, *J* = 7.4, 1H), 7.70 (d, *J* = 7.4, 1H), 7.89 (d, *J* = 4 Hz, 1H). FAB MS (m/z): 510.8 (M^+)

Synthesis of the aldehydes 8, 9, 14, and 15. Compounds, 5-[7-(4-Diphenylamino-phenyl)-benzo[1,2,5]thiadiazol-4-yl]-thiophene -2-carbaldehyde (**8),** 5-[7-(4-Diphenylamino-phenyl)-benzo[1,2,5]selenadiazol -4-yl] -thiophene-2-carbaldehyde **(9),** 5-[7-(5-Diphenylamino-thiophen-2-yl)-benzo[1,2,5] thiadiazol-4-yl]-thiophene-2-carbaldehyde (**14)** and 5-[7-(5-Diphenylamino-thiophen-2-yl) -benzo[1,2,5]selenadiazol-4-yl]-thiophene-2-carbaldehyde (**15)** were synthesized from 2-tributylstannyl-5-dioxolanylthiophene with corresponding bromides (**3, 4, 10** and **11**) by Stille coupling reactions followed by deprotection in acetic acid. Only the preparation of **8** will be described in detail.

5-[7-(4-Diphenylamino-phenyl)-benzo[1,2,5]thiadiazol-4-yl]-thiophene-2-carbalde hyde (8). To a flask containing a mixture of **3** (15 mmol, 5 g), 2-tributylstannyl-5-dioxolanyl thiophene (15 mmol, 6.7 g) and $Pd(PPh_3)Cl_2$ (250 mg) was added DMF (10mL). The reaction mixture was heated at 80 °C for 18 h, after completion it was cooled. The resulting mixture was extracted with diethylether/brine and the organic layer dried over Na_2CO_3. Evaporation of the solvent gave the crude dioxolane derivative. The resulting dioxolane derivative was suspended in glacial acetic acid (25 mL) and heated to 50 ºC. After a clear solution is formed 1 mL of water was added and maintained at 50 ºC for 5 h. It was cooled and added 50 mL ice water. The resulting orange precipitate formed was filtered and washed with water and methanol. The residue was adsorbed on silica gel and purified by column chromatography using dichloromethane/hexane mixture (1:1) as eluent to give brick red

color solid (72 %, 5.2 g). IR (CH_2Cl_2): 1667 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.06 (t, *J* = 7.4 Hz, 2H,), 7.16 - 7.18 (m, 6H), 7.23-7.30 (m, 4H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 4 Hz, 1H), 7.84 – 7.87 (m, 2H), 8.01 (d, *J* = 7.4 Hz, 1H), 8.17(d, *J* = 4Hz, 1H), 9.95 (s, 1H). ^{13}C NMR (δ, $CDCl_3$): 182.9, 153.81, 152.68, 148.9, 148.5, 147.2, 143.2, 136.7, 134.5, 130.0, 129.9, 129.4, 127.7, 127.5, 126.6, 125.1, 124.1, 123.5, 122.4. FAB MS (m/z): 489.0 (M^+)

9. Purple solid, Yield: 68 %. IR (CH_2Cl_2): 1666 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.05 (t, *J* = 7.4 Hz , 2H), 7.07-7.17 (m, 6H), 7.23-7.29 (m, 4H), 7.56 (d, J = 7.4 Hz , 1H), 7.76-7.80 (m, 3H), 7.92 (d, *J* = 7.4, 1H), 8.06 (d, *J* = 4 Hz, 1H), 9.94 (s, 1H). ^{13}C NMR (δ, $CDCl_3$): 183.0, 159.3, 158.1, 149.2, 148.4, 147.3, 143.6, 136.3, 136.1, 130.6, 130.3, 129.3, 127.9, 127.5, 127.0, 125.8, 125.0, 123.5, 122.3. FAB MS (m/z): 536.9 (M^+).

14. Purple solid, Yield: 69 %. IR (CH_2Cl_2): 1664 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 6.67 (d, 1H, *J* = 3.6 Hz), 7.08 (t, 2H, *J* = 6.5 Hz), 7.22-7.27 (m, 6H), 7.29-7.31 (m, 2H), 7.65 (d, 1H, *J* = 7.4 Hz), 7.79 (d, 1H, *J* = 3.6 Hz), 7.88 (d, 1H, *J* = 7.4 Hz), 8.02 (d, 1H, *J* = 3.5 Hz) 8.14 (d, 1H, *J* = 3.5 Hz), 9.93 (s, 1H). ^{13}C NMR (δ, $CDCl_3$): 182.8, 154.9, 152.3, 148.9, 147.3, 143.0, 136.7, 130.5, 129.3, 128.4, 127.5, 124.0, 123.6, 123.4, 123.0, 119.1. FAB MS (m/z): 495.0 (M^+).

15. Purple solid, Yield: 63 %. IR (CH_2Cl_2): 1664 cm^{-1}. ^1H NMR (δ,$CDCl_3$): 6.6 (d, *J* = 4.0 Hz, 1H), 7.07 (t, *J* = 7.4, 2 H), 7.21-7.31 (m, 8H), 7.60 (d, *J* = 7.4, 1H), 7.77 (d, *J* = 4, 1H), 7.83 (d, *J* = 7.5, 1H), 7.91 (d, *J* = 4, 1H), 8.02 (d, *J* = 4, 1H), 9.92 (s, 1H). ^{13}C NMR (δ, DMSO): 182.9, 157.85, 155.3, 149.2, 147.4, 143.3, 136.3, 131.0, 129.6, 129.3, 128.1, 127.9, 127.2, 124.6, 123.9, 123.6, 123.4, 119. FAB MS (m/z): 542.9 (M^+).

Synthesis of the dyes S1, S2, S3 and S4. Compounds 2-cyano-3-{5-[7-(4-diphenylamino-phenyl)benzo[1,2,5]thiadiazol-4-yl]–thiophen-2-yl}–acrylic acid (**S1),** 2-Cyano-3-{5-[7-(4-diphenylamino-phenyl)-benzo[1,2,5] selenadiazol-4-yl]-thiophen-2-yl}-acrylic acid (**S2),** 2-Cyano-3-{5-[7-(5-diphenylamino -thiophen-2-yl)-benzo[1,2,5]thiadiazol-4-yl]-thiophen-2-yl}-acrylic acid **(S3)** and

2-Cyano-3-{5-[7-(5-diphenylamino-thiophen-2-yl)-benzo[1,2,5]selenadiazol-4-yl]-thiophe n-2-yl}-acrylic acid (**S4**) were synthesized by similar procedures, and only the preparation of **S1** will be described in detail.

2-Cyano-3-{5-[7-(4-diphenylamino-phenyl)benzo[1,2,5]thiadiazol-4-yl]-thiophen-2-yl}-acrylic acid (S1). To a flask containing a mixture of **8** (2 mmol, 0.97 g)**,** cyanoacetic acid **(**2 mmol, 0.17g**),** ammonium acetate (0.5 mmol, 0.04g) was added acetic acid (10 ml). The mixture was heated at 120ºC for 5 h. and allowed to cool to room temperature. The resulting solid was filtered and washed with distilled water, diethyl ether and methanol to give dark brown solid (0.9 g, 81 %)**.** IR (nujol): 1709, 2214, 3416 cm^{-1}. ^{1}H NMR (δ, DMSO): 7.00-7.09 (m, 8H), 7.31 (t, *J* = 7.4, 4H), 7.83 (d, *J* = 7.4, 1H), 7.90 (d, *J* = 7.5, 2H), 8.01 (d, *J* = 3.8 Hz, 1H), 8.18-8.24 (m, 2H), 8.46 (s, 1H). ^{13}C NMR (δ, DMSO): 163.5, 152.9, 151.8, 147.8, 147.5, 146.7, 146.4, 139.8, 136.4, 133.2, 130.2, 129.6, 127.8, 127.7, 126.9, 124.7, 123.7, 123.1, 121.7, 116.4, 98.6. FAB MS(m/z): 556.0 (M^+). Anal calcd for $C_{32}H_{20}N_4O_2S_2$: C, 69.04; H, 3.62; N, 10.06%. Found: C, 68.87; H, 3.59; N, 9.88%.

S2: Dark purple solid, Yield: 87 %. IR (nujol): 1710, 2218, 3425 cm^{-1}. ^{1}H NMR (δ, DMSO): 7.05-7.10 (m, 8H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.88-7.90 (d, *J* = 7.4 Hz, 2H), 8.03 (d, *J* = 4 Hz, 1H), 8.19-8.22 (m, 2H), 8.45 (s, 1H). ^{13}C NMR (δ, DMSO): 163.2, 156.9, 156.2, 148.0, 147.3, 131.4, 131.1, 130.1, 128.1, 127.3, 125.0, 124.1, 122.5, 116.5, 98.4 FAB MS(m/z): 604.0 (M^+). Anal calcd for $C_{32}H_{20}N_4O_2SSe$: C, 63.68; H, 3.34; N, 9.28%. Found: C, 64.54; H, 3.32; N, 9.01%.

S3. Dark purple solid, Yield: 91 %. IR (nujol): 1709, 2217, 3416 cm^{-1}. ^{1}H NMR (δ, DMSO): 6.68 (d, *J* = 4 Hz, 1H), 7.12-7.20(m, 6H), 7.37(t, *J* = 7.4, 4H), 7.94 (d, *J* = 7.4, 1H), 8.02-8.05 (dd, *J* = 4Hz, 2H), 8.17-8.21 (m, 2H), 8.49 (s, 1H). ^{13}C NMR (δ, DMSO): 163.5, 154.9, 151.5, 151.2, 147.6, 146.8, 146.3, 139.8, 136.2, 129.6, 129.4, 128.1, 127.8, 127.4, 127.1, 124.2, 123.6, 123.4, 122.0, 118.3, 116.4, 98.3. FAB MS(m/z): 562.0 (M^+). Anal calcd for $C_{30}H_{18}N_4O_2S_3$: C, 64.04; H, 3.22; N, 9.96%. Found: C, 63.77; H, 3.06; N, 10.04%.

S4. Dark purple solid, Yield: 89 %. IR (nujol): 1710, 2213, 3415 cm^{-1}. ^{1}H NMR (δ, DMSO): 6.68 (d, *J* = 4 Hz, 1H), 7.10-7.18 (m, 6H), 7.36 (t, *J* = 7.4 Hz, 4H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 4 Hz, 1H), 8.02 (d, *J* = 4 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 8.17 (d, *J* = 4 Hz, 1H), 8.46 (s, 1H). ^{13}C NMR (δ, DMSO): 163.6, 156.6, 156.4, 155.3, 148.4, 147.0, 146.3, 139.4, 136.5, 130.3, 129.6, 128.5, 127.7, 127.5, 127.3, 124.0, 123.7, 123.3, 123.0, 118.5, 116.6, 98.1. FAB MS(m/z): 609.8 (M^+). Anal calcd for $C_{30}H_{18}N_4O_2S_2Se$: C, 59.11; H, 2.98; N, 9.19%. Found: C, 58.92; H, 2.94; N, 9.06%.

References

1. Pilgram, K.; Zupan. M.; Skiles, R. J. *Heterocycl. Chem,* **1970**, 7, 629.

2. Bird, C. W.; Cheeseman, G. W. H.; Sarsfield, A. A. *J. Chem. Soc.* **1963**, 4767.

3. Leung, M.-k.; Chou, M.-Y.; Su, Y. O.; Chiang, C. L.; Chen, H. –L.; Yang, C. F.; Yang, C. –C.; Lin, C. –C.; Chen, H. –T. *Org.Lett.;* **2003**, *5*, 839.

4. Wu, I.-Y.; Lin, J. T.; Tao, Y.-T.; Balasubramaniam, E.; Su, Y.-Z.; Ko, C.-W. *Chem. Mater*. **2001**, *13*, 2626

5. Prim, D.; Auffrant, A.; Plyta, Z. F.; Tranchier, J. –P.; Munch, F. R.; Rose, E. *J. Organomet. Chem.* **2001**, *624*, 124.

6. Justin Thomas, K. R.; Lin, J. T.; Velusamy, M.; Tao, Y.-T.; Chuen, C.-H. *Adv. Funct. Mater*. **2004**, *14*, 83.

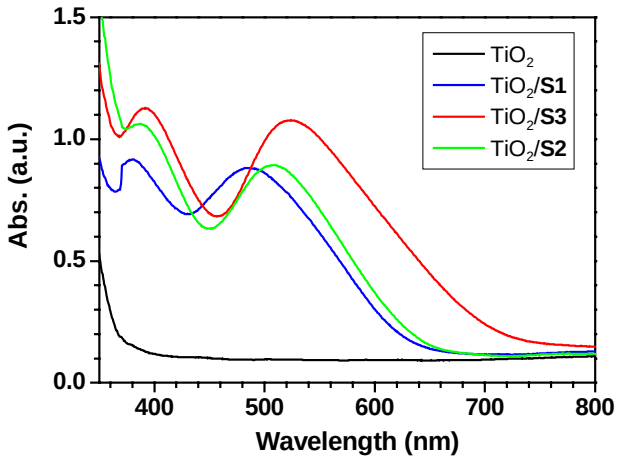

Fig. S1 Absorption spectra of the dyes adsorbed on TiO_2 film.

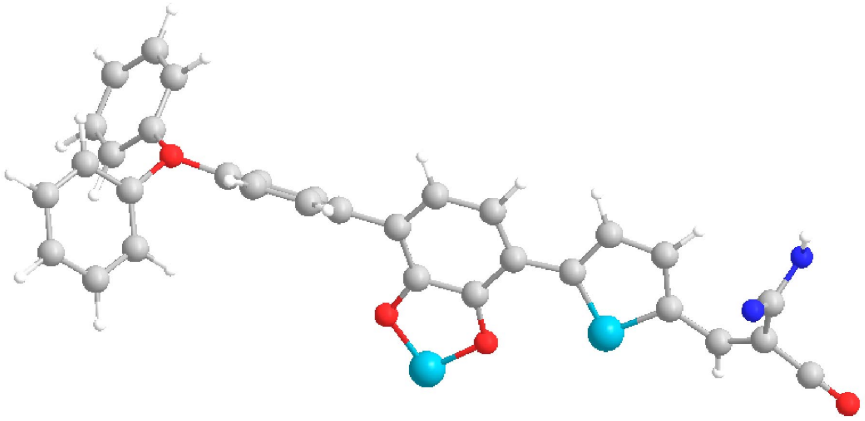

Fig. S2 Minimized geometry of S1.

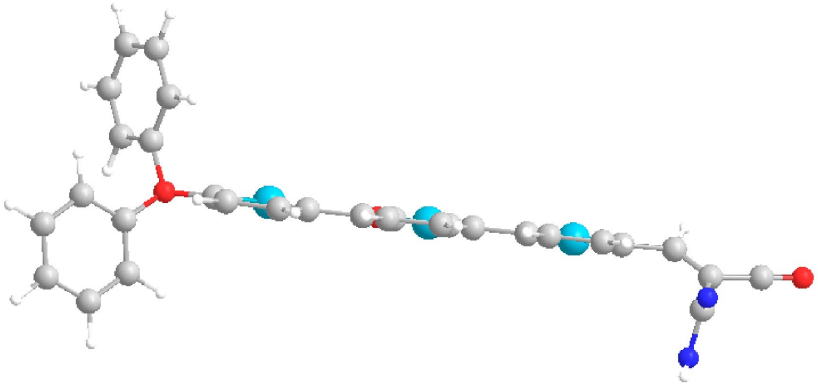

Fig S3. Minimized geometry of S3.