Functionalized Asymmetric Linear Acenes for High Performance Organic Semiconductors.

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Materials Synthesis

All chemical reagents were purchased from Aldrich Chemical Co, TCI, Lancaster, or Alfa Aesar and were used as received.

5,10,α-bromoanthra[2,3-b]thiophenedione. To an oven-dried flask were added 5,10-anthra[2,3-b]thiophenedione (1 g., 3.78 mmol., 1 equiv.) and N-bromosuccinimide (2.02 g., 11.35 mmol., 3 equiv.) in anhydrous DMF (19 mL). The reaction was stirred at RT for 24 h then quenched with DI H2O; vacuum-filtered and washed with ethanol to give a yellow powder (1.29g, 86%).

1H NMR (500MHz, CDCl3, 25ºC): δH = 8.86 (s, 1 H), 8.81 (s, 1 H), 8.39 (m, 2 H), 7.84 (m, 2 H), 7.77 (s, 1 H) ppm. MS (+ESI/ APCI) m/z: 342.94 (MH+). Elemental anal. Found: C, 55.91; H, 2.01. Calcd for C16H7BrO2S: C, 55.99; H, 2.06.

1, α-bromoanthra[2,3-b]thiophene. To a flame-dried flask were added Al wire (1.89 g., 69.93 mmol., 30 equiv.), HgCl2 (0.04 g., 0.14 mmol., 0.06 equiv.), CBr4 (0.19 g., 0.58 mmol., 0.25 equiv.) and cyclohexanol (63 mL). The reaction mixture was refluxed until a clear, colorless solution formed; cooled, and α-bromo5,10anthra[2,3-b]thiophenedione was added to the solution (0.8 g., 2.33 mmol., 1 equiv.). This was refluxed 24hrs, then cooled to RT, and stirred with 64ml of EtOH and 6M HCl(aq). This bright yellow suspension was then filtered to give yellow crystals (0.57g, 78%).

1H NMR (500MHz, CDCl3, 25ºC): δH = 8.70 (s, 1 H), 8.55 (s, 1 H), 8.53 (s, 2 H), 8.04 (m, 2 H), 7.50 (s, 1 H), 7.47 (m, 2H) ppm. 13C NMR (500MHz, [D5]Bromobenzene, 95ºC, TMS): δC =137.14, 136.36, 132.61, 132.22, 130.46, 128.82, 128.89, 128.66, 128.59, 127.78, 127.55, 126.44, 126.33, 126.07, 125.87, 107.96 ppm. MS (DEI) m/z: 312 (M+). Elemental anal. Found: C, 62.88; H, 2.22; S, 10.30; Br, 25.05. Calcd for C16H9BrS: C, 61.36; H, 2.90; S, 10.24; Br, 25.51.

5,12,α-bromotetraceno[2,3-b]thiophenedione. Into flame-dried glassware was added 5,12-tetraceno[2,3-b]thiophenedione (0.2 g., 0.64 mmol., 1 equiv.) in dry chloroform. Br2(l) (0.51 g., 3.2 mmol., 5 equiv. 0.982 mL) was added dropwise, turning the suspension a bright orange color. The reaction was stirred at RT overnight. Another 5 equiv. Br2 was added dropwise; reaction stirred at RT for 12 hrs. The reaction was then quenched with aqueous NaOH (1 M) until the aqueous layer tested basic with pH paper. The organic layer was evaporated under reduced pressure, the crude product filtered and washed with ethanol; dried overnight under vacuum to give a yellow solid (0.20g, 80%).

1H NMR (500MHz, CDCl3, 25ºC): δH =8.96 (s, 1 H), 8.95 (s, 1 H), 8.93 (s, 1H), 8.90 (s, 1H), 8.15
(m, 2 H), 7.78 (s, 1 H), 7.73 (m, 2H) ppm. MS (DEI) m/z: 394 (M+). Elemental anal. Found: C, 50.75; H, 3.86. Calcd for C_{20}H_{9}BrO_{2}S: C, 61.08; H, 2.31.

2, \(\alpha\)-bromotetraceno[2,3-b]thiophene. Prepared in the same way as 1, reddish purple powder (78%). \(^1\)H NMR (500MHz, [D\(_5\)]Bromobenzene, 95°C, TMS): \(\delta\)H =8.75 (s, 1 H), 8.61 (s, 1 H), 8.56 (s, 1 H), 8.55 (s, 1 H), 8.46 (s, 1 H), 8.27 (s, 1 H), 7.89 (m, 2 H), 7.27 (m, 2 H), 7.21 (s, 1 H) ppm. MS (+ESI/ APCI) m/z: 361.98 (M+) Elemental anal. Found: C, 63.93; H, 2.88; S, 8.32; Br, 24.67. Calcd for C\(_{20}\)H\(_{11}\)BrS: C, 66.13; H, 3.05; S, 8.83; Br, 22.00.

3, \(\alpha\)-n-hexylantra[2,3-b]thiophene. Into a two-necked round-bottom flask was added 1, \(\alpha\)-bromoanthra[2,3-b]thiophene (1.10 g, 3.51 mmol), 44ml of dioxane and Ni(1,3-Bis(diphenylphosphino)propane) dichloride (38mg, 0.070mmol). A 2M n-hexylmagnesium bromide solution in ether (3.51 ml, 7.02 mmol) was added dropwise to the solution. The mixture was then refluxed overnight, cooled to RT, quenched with DI H\(_2\)O and 1M HCl(aq) and extracted with dichloromethane. The organic extracts were then washed with brine, dried with magnesium sulfate, and the solvent removed under reduced pressure. The crude product was then flushed through a silica gel pad with hexane: dichloromethane= 20: 1 column as the eluent to yield a yellow powder (0.95g, 85%). \(^1\)H NMR (500MHz, CDCl\(_3\), 25°C): \(\delta\)H =8.63 (s, 1 H), 8.15 (s, 2 H), 8.40 (s, 1H), 8.02 (m, 2 H), 7.43 (m, 2 H), 7.12 (s, 1H), 2.94 (t, \(^3\)J (H, H) = 8 Hz, 2 H; CH\(_2\)), 1.86 (m, 2H), 1.49 (m, 2H), 1.37 (m, 4H), 0.92 (t, \(^3\)J (H, H) = 7 Hz, 3H; CH\(_3\)) ppm. \(^13\)C NMR (500MHz, CDCl\(_3\), 25°C): \(\delta\)C =139.15, 139.00, 136.49, 133.97, 131.45, 131.18, 129.68, 129.41, 128.31, 128.27, 126.74, 125.19, 125.04, 122.98, 120.85, 119.87, 31.95, 29.58, 28.90, 28.85, 22.88, 14.34 ppm. MS (+ESI/ APCI) m/z: 319.15 (MH+) Elemental anal. Found: C, 82.74; H, 7.05; S, 8.12. Calcd for C\(_{22}\)H\(_{22}\)S: C, 82.97; H, 6.96; S, 10.07.

4, \(\alpha\)-n-hexyltetraceno[2,3-b]thiophene. Into a two-necked round-bottom flask was added 2, \(\alpha\)-bromotetraceno[2,3-b]thiophene (0.94 g, 2.59 mmol), 35ml of dioxane and Pd(1,1’-Bis(diphenylphosphino)-ferrocene)dichloro Palladium complexed with dichloromethane (42mg, 0.052mmol). This flask was then bubbled with Ar(g) for 30mins. Degassed 2M n-hexylmagnesium bromide solution in ether (3.51 ml, 7.02 mmol) was added dropwise to the solution. The mixture was then refluxed overnight, cooled to RT and precipitated in degassed methanol. The crude product was refluxed in degassed acetonitrile and filtered. The residue from the filtration was a reddish-purple powder (0.74g, 78%). \(^1\)H NMR (500MHz, CDCl\(_3\), 25°C): \(\delta\)H =8.90 (s, 1 H), 8.77 (s, 1 H), 8.68 (s, 2 H), 8.50 (s, 1 H), 8.39 (s, 1 H), 7.97 (m, 2 H), 7.37 (m, 2 H), 7.09 (s, 1H), 2.93 (t, \(^3\)J (H, H) = 8 Hz, 2H; CH\(_2\)), 1.86 (m, 2H), 1.51 (m, 2H), 1.39 (m, 4H), 0.93 (t, \(^3\)J (H, H) = 7 Hz, 3H; CH\(_3\)) ppm. MS (+ESI/ APCI) m/z: 369.17 (MH+) Elemental anal. Found: C, 82.67; H, 5.63. Calcd for C\(_{26}\)H\(_{24}\)S: C, 84.74; H, 6.56.
Out-of-plane XRD

**Figure 1.** Out-of-plane XRD scan of 2, α-bromotetraceno[2,3-\(b\)]thiophene on OTS treated SiO\(_2\) and bare SiO\(_2\) at various substrate temperatures.

**Figure 2.** Out-of-plane XRD scan of 1, α-bromoanthra[2,3-\(b\)]thiophene on OTS treated SiO\(_2\) and bare SiO\(_2\) at various substrate temperatures.
Figure 3. Out-of-plan XRD scan of 3, α-n-hexylantra[2,3-b]thiophene on OTS treated SiO₂ and bare SiO₂ at various substrate temperatures.

Figure 4. Out-of-plan XRD scan of 4, α-n-hexyltetraceno[2,3-b]thiophene on OTS treated SiO₂ and bare SiO₂ at various substrate temperatures.
TFT curves

Figure 5. Typical TFT curves for 1, α-nbromoanthra[2,3-b]thiophene on OTS treated SiO\textsubscript{2} at a substrate temperature of RT.

Figure 6. Typical TFT curves for 3, α-nhexylanthra[2,3-b]thiophene on OTS treated SiO\textsubscript{2} at a substrate temperature of 40°C.
Figure 7. Typical TFT curves for 4, α-hexyltetraceno[2,3-b]thiophene on OTS treated SiO$_2$ at a substrate temperature of 40°C.