

Supplementary data

3-bromo-2-cycloheptatrienylbenzothiophene (1); mp 62~63 °C (Found: C, 59.58; H, 3.47. C₁₅H₁₁BrS requires C, 59.42; H, 3.66 %); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.84-7.76 (2H, m, six-membered ring), 7.48-7.33 (2H, m, six-membered ring), 6.78-6.75 (2H, dd, *J* 3.0, 3.0, seven-membered ring), 6.32-6.28 (2H, broad s, seven-membered ring), 5.52-5.47 (2H, dd, *J* 9.1, 5.6, seven-membered ring), 3.43 (1H, t, *J* 5.5, seven-membered ring); *m/z*: 304 (M+2) □ 302 (M⁺).

2-Cycloheptatrienyl-3-(5-methyl-2-furyl)benzothiophene (2a); pale yellow oil (Found C, 78.68; H, 5.24. C₂₀H₁₆OS requires C, 78.91; H, 5.30 %): $\delta_{\text{H}}(\text{CDCl}_3)$ 8.04 (1H, d, *J* 8.6, six-membered ring), 7.82 (1H, d, *J* 8.3, six-membered ring), 7.42-7.23 (2H, m, six-membered ring), 6.75-6.69 (2H, dd, *J* 3.0, 3.0, seven-membered ring), 6.26 (3H, broad d, *J* 3.1, seven-membered ring & furan ring), 6.03 (1H, d, *J* 2.7 Hz, furan ring), 5.54 (2H, dd, *J* 9.0, 5.5, seven-membered ring), 3.43 (1H, t, *J* 5.4, methine), 2.33 (3H, s, methyl); *m/z*: 304 (M⁺).

2-Cycloheptatrienyl-3-(5-ethyl-2-furyl)benzothiophene (2b); pale yellow oil (Found: C, 79.14; H, 5.82. C₂₁H₁₈OS requires C, 79.21; H, 5.70); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.03 (1H, d, *J* 8.4, six-membered ring), 7.83 (1H, d, *J* 8.6, six-membered ring), 7.40-7.33 (2H, m, six-membered ring), 6.73 (2H, dd, *J* 3.1, 3.0, seven-membered ring), 6.27 (3H, broad d, *J* 3.2, seven-membered ring & furan ring), 6.05 (1H, d, *J* 3.1, furan ring), 5.54 (2H, dd, *J* 8.9, 5.5, seven-membered ring), 3.46 (1H, t, *J* 5.5, methine), 2.68 (2H, q, *J* 7.3 Hz, methylene), 1.25 (3H, t, *J* 7.3, methyl); *m/z*: 318 (M⁺).

2-Cycloheptatrienyl-3-(5-pentyl-2-furyl)benzothiophene (2c); pale yellow oil (Found: C, 80.12; H, 6.58. C₂₄H₂₄OS requires C, 79.96; H, 6.71); ¹H nmr(CDCl₃): δ 8.02 (1H, d, *J* 7.5, six-membered ring), 7.83 (1H, d, *J* 7.5, six-membered ring), 7.42-7.30 (2H, m, six-membered ring), 6.73 (2H, dd, *J* 3.1, 3.0, seven-membered ring), 6.30-6.23 (3H, m, seven-membered ring and furan ring), 6.05 (1H, d, *J* 3.2, furan ring), 5.54 (2H, dd, *J* 9.1, 5.4, seven-membered ring), 3.46 (1H, t, *J* 5.4, methine), 2.64 (1H, d, *J* 7.4, methylene), 1.60 (2H, m, methylene), 1.35 (4H, m, methylene), 0.90 (3H, t, *J* 7.3, methyl); *m/z* 360 (M⁺).

2-Cycloheptatrienyl-3-(5-octadecyl-2-furyl)benzothiophene (2d); pale yellow oil (Found:

C,81.66; H, 9.45. C₃₇H₅₀OS requires C,81.86; H, 9.28); ¹H nmr(CDCl₃): δ 8.03 (1H, d, *J* 7.5, six-membered ring), 7.85 (1H, d, *J* 7.5, six-membered ring), 7.43-7.28 (2H, m, six-membered ring), 6.73 (2H, dd, *J* 3.0, 3.0, seven-membered ring), 6.32-6.25 (3H, m, seven-membered ring & furan ring), 6.04 (1H, d, *J* 3.2, furan ring), 5.53 (2H, dd, *J* 9.1, 5.3, seven-membered ring), 3.48 (1H, t, *J* 5.3, methine), 2.72 (2H, t, *J* 6.8, methylene), 1.78-1.35 (32H, m, methylene), 0.92 (3H, t, *J* 7.2, methyl); *m/z* 542 (M⁺).

2-Cycloheptatrienyl-3-(5-phenyl-2-furyl)benzothiophene (2e); pale yellow oil (Found: C,82.02; H, 4.77. C₂₅H₁₈OS requires C,81.94; H, 4.95 %); δ_H (CDCl₃) 8.03 (1H, d, *J* 7.5, six-membered ring), 7.82 (1H, d, *J* 7.5, six-membered ring), 7.45-7.33 (4H, m, six-membered ring & phenyl), 7.30-7.02 (3H, m, phenyl), 6.70 (2H, dd, *J* 3.0, 3.0, seven-membered ring), 6.48 (1H, d, *J* 3.5, furan ring), 6.22 (1H, d, *J* 3.5, furan ring), 6.14 (2H, broad d, *J* 9.1, seven-membered ring), 5.36(2H, dd, *J* 9.1, 5.5, seven-membered ring), 3.48 (1H, t, *J* 5.5, methine); *m/z*: 366 (M⁺).

2-Cycloheptatrienyl-3-[5-(1,3-dioxolan-2-yl)-2-furyl]benzothiophene (2f); pale yellow oil (Found: C,72.72; H, 5.27. C₂₂H₁₈O₃S requires C,72.91; H, 5.01 %); δ_H (CDCl₃) 8.01 (1H, d, *J* 7.6, six-membered ring), 7.80 (1H, d, *J* 7.2, six-membered ring), 7.38-7.28 (2H, m, six-membered ring), 6.72-6.70 (2H, m, seven-membered ring), 6.48 (1H, d, *J* 3.2, furan ring), 6.33 (1H, d, *J* 3.2, furan ring), 6.26-6.22 (2H, m, seven-membered ring), 5.96 (1H, s, methine), 5.52 (2H, dd, *J* 9.0, 5.5, seven-membered ring), 4.12-4.07 (2H, m, dioxolane ring), 3.99-3.93 (2H, m, dioxolane ring), 3.43 (1H, t, *J* 5.5, methine); *m/z*: 362 (M⁺);.

2-Cycloheptatrienyl-3-(5-formyl-2-furyl)benzothiophene (2g); pale yellow oil (Found: C,75.58; H, 4.63. C₂₀H₁₄O₂S requires: C,75.45; H, 4.43 %.); δ_H (CDCl₃) 9.65 (1H, s, formyl), 8.13 (1H, d, *J* 7.5, six-membered ring), 7.85 (1H, d, *J* 7.5, six-membered ring), 7.48-7.34 (2H, m, six-membered ring), 7.29 (1H, d, *J* 3.7 Hz, furan ring), 6.77 (2H, dd, *J* 3.1, 3.0, seven-membered ring), 6.54 (1H, d, *J* 3.7, furan ring), 6.32-6.27 (2H, m, seven-membered ring), 5.54-5.49 (2H, dd, *J* 9.0, 5.5, seven-membered ring), 3.38 (1H, t, *J* 5.5, methine); *m/z*: 318 (M⁺).

2-Cycloheptatrienyl-3-[5-(phenylimino)methyl-2-furyl]benzothiophene (2h); mp 136-137 °C (Found: C,79.56; H, 4.94. C₂₆H₁₉NOS requires C,79.36; H, 4.87 %); δ_H (CDCl₃) 8.32 (1H, s, -CH=N),

8.14 (1H, d, *J* 7.5, six-membered ring), 7.86 (1H, d, *J* 7.5, six-membered ring), 7.45-7.37 (4H, m, six-membered ring & phenyl), 7.25-7.23 (3H, m, phenyl), 7.10 (1H, d, *J* 3.5, furan ring), 6.78-6.67 (2H, dd, *J* 3.1, 3.0, seven-membered ring), 6.55 (1H, d, *J* 3.1, furan ring), 6.33-6.29 (2H, m, seven-membered ring), 5.59-5.53 (2H, dd, *J* 9.1, 5.4, seven-membered ring), 3.46 (1H, t, *J* 5.4, methine); *m/z*: 393 (M^+).

3-Bromo-2-(5-methyl-2-furyl)benzothiophene (5a); mp 95 °C (Found: C,53.31; H, 3.14. $C_{13}H_9BrOS$ requires C,53.26; H, 3.09 %); δ_H ($CDCl_3$) 7.80-7.75 (2H, m, six-membered ring), 7.45-7.33 (2H, m, six-membered ring), 7.19 (1H, d, *J* 3.4, furan ring), 6.16 (1H, d, *J* 3.4, furan ring), 2.39 (3H, s, methyl); *m/z*: 294 ($M+2$), 292 (M^+).

3-Bromo-2-(5-ethyl-2-furyl)benzothiophene (5b); mp 42 °C (Found: C,54.92; H, 3.51. $C_{14}H_{11}BrOS$ requires C,54.74; H, 3.61 %); δ_H ($CDCl_3$) 7.82-7.75 (2H, m, six-membered ring), 7.43-7.28 (2H, m, six-membered ring), 7.18 (1H, d, *J* 3.4, furan ring), 6.16 (1H, d, *J* 3.4, furan ring), 2.72 (2H, q, *J* 7.4, methylene), 1.26 (3H, t, *J* 7.4 Hz, methyl); *m/z*: 308 ($M+2$), 306 (M^+);.

3-Cycloheptatrienyl-2-(5-methyl-2-furyl)benzothiophene (6a); mp 95 °C (Found: C,79.15; H, 5.43. $C_{20}H_{16}OS$ requires C,78.91; H, 5.30 %); δ_H ($CDCl_3$) 7.85-7.80 (2H, m, six-membered ring), 7.34-7.28 (2H, m, six-membered ring), 6.73 (2H, dd, *J* 3.1, 3.1, seven-membered ring), 6.26 (3H, broad d, *J* 3.3, seven-membered ring & furan ring), 6.01 (1H, d, *J* 2.9, furan ring), 5.62-5.56 (2H, dd, *J* 9.0, 5.3, seven-membered ring), 3.71 (1H, t, *J* 5.3, methine), 2.31 (3H, s, methyl); *m/z*: 304 (M^+).

3-Cycloheptatrienyl-2-(5-ethyl-2-furyl)benzothiophenes (6b); mp 64°C (Found: C,79.38; H, 5.54. $C_{21}H_{18}OS$ requires C,79.21; H, 5.70 %); δ_H ($CDCl_3$) 7.85-7.80 (2H, m, six-membered ring), 7.35-7.29 (2H, m, six-membered ring), 6.73 (2H, dd, *J* 3.1, 3.0, seven-membered ring), 6.33 (1H, d, *J* 3.2, furan ring), 6.26 (2H, broad s, seven-membered ring), 6.01 (1H, d, *J* 3.5, furan ring), 5.62-5.57 (2H, dd, *J* 9.1, 5.3, seven-membered ring), 3.75 (1H, t, *J* 5.3, methine), 2.64 (2H, q, *J* 7.5, methylene), 1.21 (3H, t, *J* 7.5, methyl); *m/z*: 318 (M^+);.