Supporting Information

Tripodal Binding Units for Self-Assembled Monolayers on Gold: A Comparison of Thiol and Thioether Headgroups

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NMR-Spectroscopic Characterization and Elemental Analyses of 1a, 1b, 2a, 2b, PTT, and BPTT:

NMR experiments: The ^{1}H, $^{13}C\{^{1}H\}$, and $^{29}Si\{^{1}H\}$ NMR spectra were recorded at 23 °C on a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) or a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz). $CDCl_3$ was used as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24), $CDCl_3$ (^{13}C, δ 77.0), or external TMS (^{29}Si, δ 0). Analysis and assignment of the ^{1}H NMR data were supported by $^{1}H,^{1}H$ COSY, $^{13}C,^{1}H$ HMQC, and $^{13}C,^{1}H$ HMBC experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135, $^{13}C,^{1}H$ HMQC, and $^{13}C,^{1}H$ HMBC experiments.

Elemental analyses: The elemental analyses were performed by using an Elementar VarioMicro system.

*Tris(chloromethyl)phenylsilane (**1a**)*

^{1}H NMR (300,1 MHz, $CDCl_3$): δ 3.29 (s, 6 H, C*H*$_2$), 7.40–7.49 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.65–7.68 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.5 (*C*H$_2$), 128.4 (*C*-3/*C*-5, C_6H_5), 131.2 (*C*-4, C_6H_5), 134.0 (*C*-1, C_6H_5), 134.6 (*C*-2/*C*-6, C_6H_5). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ –8.2. Anal. calcd for $C_9H_{11}Cl_3Si$: C, 42.62; H, 4.37. The elemental analysis could not be performed due to the high chlorine content (> 40%) of **1a**.

*(4-Biphenyl)tris(chloromethyl)silane (**1b**)*

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.32 (s, 6 H, C*H*$_2$), 7.34–7.40 (m, 1 H, *H*-4, C_6H_5), 7.42–7.48 (m, 2 H, *H*-3/*H*-5, C_6H_5), 7.57–7.61 (m, 2 H, *H*-2/*H*-6, C_6H_5), 7.64–7.67 (m, 2 H, *H*-2/*H*-6, C_6H_4), 7.73–7.76 (m, 2 H, *H*-3/*H*-5, C_6H_4). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.5 (*C*H$_2$), 127.0 (*C*-4, C_6H_4), 127.1 and 127.2 (*C*-2/*C*-6, C_6H_5; *C*-2/*C*-6, C_6H_4), 127.9 (*C*-4, C_6H_5), 128.9 (*C*-3/*C*-5, C_6H_5), 135.1 (*C*-3/*C*-5, C_6H_4), 140.4 (*C*-1, C_6H_5), 144.0 (*C*-1, C_6H_4). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ –8.0. Anal. calcd for $C_{15}H_{15}Cl_3Si$: C, 54.64; H, 4.59. Found: C, 54.8; H, 4.5.

*Tris(acetylthiomethyl)phenylsilane (**2a**)*

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.30 (s, 9 H, C*H*$_3$), 2.47 (s, 6 H, C*H*$_2$), 7.33–7.43 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.47–7.52 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 9.8 (*C*H$_2$), 30.1 (*C*H$_3$), 128.2 (*C*-3/*C*-5, C_6H_5), 130.7 (*C*-4, C_6H_5), 131.1 (*C*-1, C_6H_5), 134.1 (*C*-2/*C*-6, C_6H_5), 195.4 (*C*=O). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ –4.8. Anal. calcd for $C_{15}H_{20}O_3S_3Si$: C, 48.35; H, 5.41; S, 25.82. Found: C, 48.4; H, 5.4; S, 26.2.

*Tris(acetylthiomethyl)(4-biphenyl)silane (**2b**)*

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.31 (s, 9 H, C*H*$_3$), 2.51 (s, 6 H, C*H*$_2$), 7.31–7.37 (m, 1 H, *H*-4, C_6H_5), 7.40–7.46 (m, 2 H, *H*-3/*H*-5, C_6H_5), 7.56–7.63 (m, 6 H, *H*-2/*H*-6, C_6H_5, *H*-2/*H*-3/*H*-5/*H*-6, C_6H_4). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 9.8 (*C*H$_2$), 30.0 (*C*H$_3$), 126.8 and 127.0 (*C*-2/*C*-6, C_6H_5, *C*-2/*C*-6, C_6H_4), 127.7 (*C*-4, C_6H_5), 128.8 (*C*-3/*C*-5, C_6H_5), 129.7 (*C*-4, C_6H_4), 134.6 (*C*-3/*C*-5, C_6H_4), 140.3 (*C*-1, C_6H_5), 143.3 (*C*-1, C_6H_4), 195.3 (*C*=O). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ –4.7. Anal. calcd for $C_{21}H_{24}O_3S_3Si$: C, 56.21; H, 5.39; S, 21.44. Found: C, 55.9; H, 5.3; S, 22.2.

*Tris(mercaptomethyl)phenylsilane (**PTT**)*

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.31 (t, $^{3}J_{HH}$ = 7.5 Hz, 3 H, S*H*), 2.13 (d, $^{3}J_{HH}$ = 7.5 Hz, 6 H, C*H*$_2$), 7.38–7.46 (m, 3 H, *H*-3/*H*-4/*H*-5, C_6H_5), 7.55–7.60 (m, 2 H, *H*-2/*H*-6, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 2.72 (*C*H$_2$), 128.4 (*C*-3/*C*-5, C_6H_5), 130.6 (*C*-4, C_6H_5), 131.0 (*C*-1, C_6H_5), 134.5 (*C*-2/*C*-6, C_6H_5). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ –2.3. Anal. calcd for $C_9H_{14}S_3Si$: C, 43.85; H, 5.72; S, 39.03. Found: C, 43.8; H, 5.4; S, 39.3.

*(4-Biphenyl)tris(mercaptomethyl)silane (**BPTT**)*

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.36 (t, $^{3}J_{HH}$ = 7.5 Hz, 3 H, S*H*), 2.16 (d, $^{3}J_{HH}$ = 7.5 Hz, 6 H, C*H*$_2$), 7.34–7.38 (m, 1 H, *H*-4, C_6H_5), 7.42–7.49 (m, 2 H, *H*-3/*H*-5, C_6H_5), 7.58–7.61 (m, 2 H, *H*-2/*H*-6, C_6H_5), 7.63–7.67 (m, 4 H, *H*-2/*H*-3/*H*-5/*H*-6, C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 2.80 (*C*H$_2$), 127.06 and 127.13 (*C*-2/*C*-6, C_6H_5, *C*-2/*C*-6, C_6H_4), 127.8 (*C*-4, C_6H_5), 128.9 (*C*-3/*C*-5, C_6H_5), 129.6 (*C*-4, C_6H_4), 135.0 (*C*-3/*C*-5, C_6H_4), 140.5 (*C*-1, C_6H_5), 143.4 (*C*-1, C_6H_4). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ –2.5. Anal. calcd for $C_{15}H_{18}S_3Si$: C, 55.85; H, 5.62; S, 29.82. Found: C, 55.6; H, 5.5; S, 29.9.

Selected Crystallographic Data for BPTT:

Single crystal of dimensions 0.202 × 0.150 × 0.045 mm obtained by crystallization from *n*-hexane/diethyl ether (20:9 (v/v)) at –20 °C, $C_{15}H_{18}S_3Si$, M_r = 322.56, analysis at 100(2) K, triclinic, space group $P\bar{1}$ (no. 2), a = 7.3288(3), b = 12.9975(5), c = 17.1071(6) Å, α = 97.650(2), β = 97.306(2), γ = 90.558(2)°, V = 1601.35(11) Å^3, Z = 4, ρ_{calcd} = 1.338 g cm^{-1}, μ = 0.522 mm^{-1}, F(000) = 680, $2\theta_{max}$ = 66.76°, 86196 collected reflections, 12267 unique reflections (R_{int} = 0.0429). 349 parameters, S = 1.038, R_1 = 0.0341 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1033, max./min. residual electron density +0.793/–0.767 e Å^{-3}.