SUPPORTING INFORMATION

for the paper

Tridentate Benzylthiols on Gold(111):
Control of Self-Assembly Geometry

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Figure S11. STM images of 1-octanethiol deposited from 0.1M DMF solution. (a) Low resolution and (b) high resolution STM images (a): 59×59 nm; (b): 20×20 nm; $V_t = 700$ mV, $I_t = 0.1$ nA of $\text{C}_8\text{SH}$ SAMs on Au(111). The white arrow in figure (a) indicates an etch pit in $\text{C}_8\text{SH}$ SAMs.

Figure S12. DFT (B3LYP/6-31G(d)) calculated molecular dimensions of $\text{Me}_3$-BTMT and $\text{Et}_3$-BTMT.
Figure SI3. Interconversion between syn and anti conformers of Et₃-BTMT calculated at B3LYP/6-31G(d) level. Scan coordinate corresponds to the C-C-C-S dihedral angle (°); all other coordinate were allowed to fully relax.

Figure SI4. Pair correlation analysis of the nearest three-point contacts determined for monolayers of: a) Me₃-BTMT, b) Et₃-BTMT and 3) ODe₃-BTMT. Relative orientations of all possible trios of molecules (manually determined from high-contrast spots in STM images) was plotted in the same coordinates, providing both the average intermolecular distances and the relative orientation of two contacts emanating from the same origin (an angle of a “local unit cell”). Intermolecular separations larger than 1.6 nm (for Me₃-BTMT and Et₃-BTMT) and 3 nm (for ODe₃-BTMT) were excluded from the analysis. The red color for molecular positions and “unit cell” vectors bars correspond to intermolecular separations that are only possible for standing up orientation of molecules (<0.9 nm for Me₃-BTMT and <1.0 nm for Et₃-BTMT). Green color for molecular separations and average “unit cell vectors” represent distances at which the neighboring molecules can either lie down or stand up on the surface. The other colors do not bear any internal assignment. Average “unit cells” were: (a) a=0.5±0.2 nm, b=1.1±0.4 nm, α =80°±10°; (b) a=0.7±0.2 nm, b=1.0±0.3 nm, α=73°±20°; a=0.9±0.2 nm, b=1.1±0.3 nm, α =75°±20°; (c) a=1.7±0.5 nm, b=2.5±0.5 nm, α =75°±20°.
Synthesis.

1,3,5-Trimethyl-2,4,6-tris(chloromethyl)benzene. To a one-neck round-bottom flask equipped with a stir bar were added mesitylene (21.6 g, 0.180 mol), paraformaldehyde (32.4 g, 1.08 mol), concentrated hydrochloric acid (156 g, 1.58 mol) and sodium chloride (5.61 g, 0.100 mol). A cooler condenser was connected to the flask, and the mixture was refluxed for 12 h under vigorous stirred. After cooling down to r.t., the liquid part was decanted, and another portions of paraformaldehyde (32.4 g, 1.08 mol), concentrated hydrochloric acid (156 g, 1.58 mol), sodium chloride (5.61 g, 0.100 mol), and zinc chloride (24.6 g, 0.180 mol) were added to the reaction mass. The mixture was refluxed for another 24 h under vigorous stirring. After cooling to room temperature, the precipitate was filtered and washed a several times with water and concentrated under reduced pressure. The crude material was recrystallized from dichloromethane/toluene mixture to give the desired product (22.8 g, 48%) with NMR spectral data identical to that previously reported.1

1,3,5-Trimethyl-2,4,6-tris(S-acetylthiomethyl)benzene. 1,3,5-trimethyl-2,4,6-tris(chloromethyl)benzene (1.0 g, 3.8 mmol) and potassium thioacetate (3.0 g, 26 mol) were dissolved in DMF (10 mL) and stirred at r.t. for 4 h. The reaction mixture was poured into water (100 mL), resulting in significant precipitation. The solid material was collected by filtration, washed with H2O (200 mL), and dried under reduced pressure to give the desired product as yellow powder (1.42 g, 98%). 1H NMR (300 MHz, DMSO-d6): δ = 4.15 (6H, s), 2.36 (9H, s), 2.20 (9H, s).

1,3,5-Trimethyl-2,4,6-tris(hydrothiomethyl)benzene [Me3-BTMT]. 1,4-Dioxane and distilled H2O were purged with bubbling N2 before use. In a 50 mL two-neck round-bottom flask equipped with a stir bar, 1,3,5-trimethyl-2,4,6-tris(S-acetylthiomethyl)benzene (0.250 g, 0.65 mmol) was dissolved in 1,4-dioxane (15 mL). The flask was equipped with a condenser and a rubber septum, and the system was flushed with N2 gas for ~30 min. Sodium hydroxide (0.143 g, 3.58 mmol) was dissolved in H2O (1 mL) and added dropwise to the solution at r.t. The mixture was refluxed under N2 for 2 h and then cooled to r.t. 2M HCl (2.1 mL, 4.2 mmol) was added dropwise, and the mixture was stirred at r.t. for 1 h under N2. H2O was added, and the product was extracted with chloroform. The organic layer was washed with H2O several times and dried over MgSO4, followed by filtration and solvent evaporation to give the desired product as a white powder (0.165 g, 98%). NMR spectral data is identical to that reported earlier.2

1,3,5-Triethyl-2,4,6-tris(bromomethyl)benzene. To a 250 mL one-neck round-bottom flask equipped with a stir bar were added 1,3,5-triethylbenzene (3.93 g, 24.2 mmol), paraformaldehyde (8.75 g, 292 mmol), zinc bromide (9.69 g, 43.0 mmol), and 33% wt hydrogen bromide solution in acetic acid (55 mL; 0.30 mol). A cooler condenser was connected to the flask, and the mixture was heated to 100°C for 22 h under vigorous stirred. The mixture dissolved completely once heated, and in 3 h no precipitate was observed. Overnight heating resulted in formation of a precipitate, indicating that the reaction has completed. After cooling to room temperature, the precipitate was filtered and washed several times with water (400 mL). To remove possible zinc residues, the crude product was suspended in 1.5 M HCl (14 mL conc. HCl in 100 mL H2O) and kept under stirring for 30 min. The solid product was filtered, washed with water until the wash solution had a neutral pH, then resuspended in 0.5 M aqueous NaHCO3 (5.336 g in 100 mL H2O) and kept stirred for 20 min. The material was filtered, washed with H2O until neutral pH, and dried under reduced pressure to give the desired product as a white

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powder (9.99 g, 93%). m.p.=168–169°C. 1H NMR (400 MHz, CDCl3): δ = 4.58 (6H, s), 2.94 (6H, q, J = 7.6 Hz), 1.35 (9H, t, J = 7.6 Hz). 13C NMR (75 MHz, CDCl3): δ = 144.97, 132.63, 28.56, 22.73, 15.62.

1,3,5-Triethyl-2,4,6-tris(S-acetylthiomethyl)benzene. In a 250 mL one-neck round-bottom flask equipped with a stir bar, potassium thioacetate (9.09 g, 79.6 mmol) was dissolved in dimethylformamide (100 mL). 1,3,5-Triethyl-2,4,6-tris(bromomethyl)benzene (4.95 g, 11.2 mmol) was added to this solution and stirred at room temperature under N2 for 3 h. The reaction mixture was poured into water (200 mL) and the resulting precipitate was collected by filtration, washed with H2O, and dried under reduced pressure to give the pure product as a white powder (4.74 g, 99%). m.p.=148–149°C. 1H NMR (400 MHz, CDCl3): δ = 4.17 (6H, s), 2.60 (6H, q, J = 7.6 Hz), 2.36 (9H, s), 1.22 (9H, t, J = 7.6 Hz). 13C NMR (75 MHz, CDCl3): δ = 196.03, 143.15, 130.24, 30.32, 28.42, 23.29, 15.68. m/z (ESI+ HRMS) for C21H30O3S3: 449.1249 (M+Na)+, found 449.1240.

1,3,5-Triethyl-2,4,6-tris(hydrothiomethyl)benzene) [Et3-BTMT]. 1,4-Dioxane and distilled H2O were purged with bubbling Ar before use. In a 100 mL two-neck round-bottom flask equipped with a stir bar, 1,3,5-Triethyl-2,4,6-tris(S-acetylthiomethyl)benzene (0.716 g, 1.68 mmol) was dissolved in 1,4-dioxane (50 mL). The flask was equipped with a condenser and a rubber septum, and the system was flushed with Ar gas for ~30 min. Sodium hydroxide (0.393 g, 9.82 mmol) was dissolved in H2O (3 mL) and added dropwise to the solution at r.t. The mixture was refluxed under Ar for 3 h, then cooled to r.t. 2M HCl (5 mL, 10.0 mmol) was added dropwise, and the mixture was stirred at r.t. for 1 h under Ar. H2O was added, and the product was extracted with chloroform. The organic layer was washed with H2O several times and dried over MgSO4, followed by filtration and solvent evaporation to give the desired product as a white powder (0.504 g, 100%). 1H NMR (400 MHz, CDCl3): δ = 3.76 (6H, d, J = 6.4 Hz), 2.86 (6H, q, J = 7.6 Hz), 1.70 (3H, t, J = 6.2 Hz), 1.27 (9H, t, J = 7.6 Hz). 13C NMR (75 MHz, CDCl3): δ = 140.21, 135.48, 22.81, 22.77, 16.12.

1,3,5-Tris(acetyloxy)benzene. Acetic anhydride (70 mL, 0.7 mol) was added to a solution of phloroglucinol dihydrate (11.89 g, 73 mmol) in pyridine (50 mL) at r.t. under vigorous stirring. [Note: exothermic reaction!] In 1.5 h, ice (ca. 400 mL) was added to the reaction mixture resulting in formation of precipitate, and stirring continued for another 1 h to destroy the excess Ac2O. The resulting solid material was filtered, washed with H2O, and dried under reduced pressure to afford 1,3,5-tris(acetyloxy)benzene (17.01 g) as a light gray powder. Yield: 93%. m.p.=105–106°C. 1H NMR (300 MHz, CDCl3): δ = 6.84 (3H, s), 2.28 (9H, s). 13C NMR (75 MHz, CDCl3): δ = 168.56, 151.07, 112.75, 21.08.

1,3,5-Tris(decyloxy)benzene [ODE3-B]. In a 500 mL one-neck round-bottom flask equipped with a stir bar, 1-bromodecane (40 mL, 190 mmol) was added to a solution of 1,3,5-tris(acetyloxy)benzene (13.4 g, 50 mmol) in DMF (150 mL) at -5°C under vigorous stirring. 60% NaH in mineral oil (17.9 g, 440 mmol) was added in one portion, and the reaction mixture was stirred for 20 min, followed by addition of H2O (6 mL) at -5°C dropwise over a period of 1 h. [Note: because of released H2, it is important to use a relatively large volume flask as used here.] The reaction mixture was allowed to slowly warm to heat to r.t and kept under vigorous stirring overnight. After 21 h, the reaction mixture was heated to 50°C and stirred for another 2 h. Brine was added, and the product was extracted into ethyl acetate. The organic layer was washed with H2O and concentrated under reduced pressure to afford a crude product consisting of target material and excess of 1-bromodecane, which was removed by distillation using Büchi Glass Oven B-585 under reduced pressure (0.25 mbar) at 100°C. The residue from the reaction flask was filtered through silica gel using hexane as an eluent, affording 1,3,5-tris(decyloxy)benzene as a light yellow liquid (16.21 g, 56%). The compound contains an impurity of mineral oil (from
NaH) and can be used as is in further synthesis. For analytical purposes, it was purified by column chromatography (SiO₂; hexane – hexane/CH₂Cl₂ (2:1) gradient). ¹H NMR (300 MHz, CDCl₃): δ = 6.06 (3H, s), 3.90 (6H, t, J = 6.6 Hz), 1.75 (6H, p), 1.52–1.20 (42H, m), 0.88 (9H, t, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃): δ = 160.93, 93.72, 67.99, 31.91, 29.59, 29.57, 29.39, 29.33, 29.25, 26.06, 22.69, 14.13. m/z (ESI⁺ HRMS) for C₃₆H₆₆O₃: 547.50847 (M+H)⁺, found 547.50915.

1,3,5-Tris(decyloxy)-2,4,6-tris(bromomethyl)benzene. To a 100 mL one-neck round-bottom flask equipped with a stir bar were added 1,3,5-tris(decyloxy)benzene (2.97 g, 5.43 mmol), paraformaldehyde (2.57 g, 85.7 mmol), zinc bromide (2.30 g, 10.2 mmol), and 33% wt hydrogen bromide solution in acetic acid (20 mL; 110 mmol). A condenser was connected to the flask, and the mixture was heated to 55°C for 91 h under vigorous stirring. A higher temperature should be avoided; a partial dealkylation was observed when the reaction was performed at~70°C. The reaction mass was cooled to room temperature, H₂O was added, and the product was extracted to ethyl acetate. The organic layer was washed with H₂O until the solution was at neutral pH, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica using hexane and dichloromethane to afford the desired product as a colorless oil (0.71 g, 16%). ¹H NMR (300 MHz, CDCl₃): δ = 4.58 (6H, s), 4.25 (6H, t, J = 6.9 Hz), 1.93 (6H, p, J = 6.9 Hz), 1.6–1.2 (42H, m), 0.89 (9H, t, J = 6.8 Hz). ¹³C NMR (75 MHz, CDCl₃): δ = 159.50, 123.15, 75.04, 31.91, 30.31, 29.61, 29.58, 29.50, 29.34, 25.82, 23.11, 22.71, 14.15.

1,3,5-Tris(decyloxy)-2,4,6-tris(S-acetylthiomethyl)benzene. In a 10 mL one-neck round-bottom flask equipped with a stir bar, potassium thioacetate (97 mg, 0.85 mmol) was dissolved in dimethylformamide (1 mL) and mixed with 1,3,5-tris(decyloxy)-2,4,6-tris(bromomethyl)benzene (71 mg, 0.090 mmol) dissolved in dimethylformamide (1 mL). The reaction mixture was stirred at room temperature for 2 days. H₂O was added, and the product was extracted to chloroform. The organic layer was washed with H₂O and the solution was at neutral pH, dried over MgSO₄, filtered and concentrated under reduced pressure to afford the desired product as a yellow oil (51 mg, 75%). ¹H NMR (300 MHz, CDCl₃): δ = 4.17 (6H, s), 3.79 (6H, t, J = 6.8 Hz), 2.33 (9H, s), 1.80 (6H, p), 1.51–1.21 (42H, m), 0.89 (9H, t). ¹³C NMR (75 MHz, CDCl₃): δ = 195.37, 157.84, 120.37, 75.40, 31.92, 30.24, 30.22, 29.62, 29.58, 29.52, 29.35, 25.89, 23.41, 22.70, 14.14. m/z (ESI⁺ MS) for C₄₅H₇₈O₆S₃: 833.4858 (M+Na)+, found 833.4852.

1,3,5-Tris(decyloxy)-2,4,6-tris(hydrothiomethyl)benzene \[\text{ODE₃-BTMT}\]. 1,4-Dioxane and distilled H₂O were degassed with bubbling Ar before use. In a 100 mL two-neck round-bottom flask equipped with a stir bar, 1,3,5-tris(decyloxy)-2,4,6-tris(S-acetylthiomethyl)benzene (0.90 g, 1.1 mmol) was dissolved in 1,4-dioxane (15 mL). The flask was equipped with a condenser and a rubber septum, and the system was flushed with N₂ for ~30 min. 2.9 M aqueous sodium hydroxide (2.3 mL, 6.7 mmol) was added dropwise to the reaction at r.t. The mixture was refluxed under N₂ for 2 h, then cooled to r.t. 2M HCl (3.8 mL, 7.6 mmol) was added dropwise, and the mixture was stirred at r.t. for 1 h under nitrogen. H₂O was added, and the product was extracted with dichloromethane. The organic layer was washed with H₂O several times and dried over MgSO₄, followed by filtration and solvent evaporation to yield the desired product as a light yellow oil (0.64 g, 84%). ¹H NMR (300 MHz, CDCl₃): δ = 3.95 (6H, t, J = 6.6), 3.69 (6H, d, J = 7.8 Hz), 2.23 (3H, t, J = 7.8 Hz), 1.86 (6H, p, J = 7.2 Hz), 1.6–1.2 (42H, m), 0.89 (9H, t, J = 6.5 Hz). ¹³C NMR (75 MHz, CDCl₃): δ = 155.49, 125.73, 75.15, 31.87, 30.44, 29.57, 29.55, 29.49, 29.30, 26.03, 22.66, 18.18, 14.10. m/z (APCI⁻ HRMS) for C₃₉H₇₂O₃S₃: 683.45708 (M–H)⁻, found 683.45550.
Spectral data.

$^1$H NMR (DMSO-d$_6$, 300 MHz)

Figure S15. $^1$H NMR spectrum of 1,3,5-trimethyl-2,4,6-tris(S-acetylthiomethyl)benzene.
Figure S16. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-triethyl-2,4,6-tris(bromomethyl)benzene.
Figure S17. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-triethyl-2,4,6-tris(S-acetylthiomethyl)benzene.
**Figure S18.** Mass spectrum of 1,3,5-triethyl-2,4,6-tris(S-acetylthiomethyl)benzene.
Figure S19. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-triethyl-2,4,6-tris(hydrothiomethyl)benzene) [Et$_3$-BTMT].
Figure S110. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-tris(acetyloxy)benzene.
Figure SI11. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-tris(decyloxy)benzene.
Figure S12. Mass spectrum of 1,3,5-tris(decyloxy)benzene.
Figure SI13. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-tris(decyloxy)-2,4,6-tris(bromomethyl)benzene.
Figure S14. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-tris(decyloxy)-2,4,6-tris(S-acetylthiomethyl)benzene.
Figure SI15. Mass spectrum of 1,3,5-tris(decyloxy)-2,4,6-tris(S-acetylthiomethyl)benzene.
Figure S116. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,3,5-tris(decyloxy)-2,4,6-tris(hydrothiomethyl)benzene [ODE$_3$-BTMT].
Figure SI17. Mass spectrum of 1,3,5-tris(decyloxy)-2,4,6-tris(hydrothiomethyl)benzene.