“Cooperative Reorganization of Mineral and Template
during Directed Nucleation of Calcium Carbonate”

Supplementary Information

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1. SYNTHESIS OF MDBA MOLECULES

General Methods: Reagents were purchased from Aldrich or synthesized as described. Anhydrous triethylamine was subjected to 3 cycles of freeze-pump-thaw prior to use. Thin-layer chromatography (TLC) was carried out using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV-light. Melting points were determined on an Electrothermal MEL-TEMP 3.0 apparatus and are uncorrected. Proton and carbon nuclear magnetic resonance spectra (\(^1\)H-NMR and \(^{13}\)C-NMR) spectra were recorded on a Bruker Avance II 500 using deuterated solvent as lock and the residual solvent as internal standard. All chemical shifts are quoted using the \(\delta\) scale, and all coupling constants (\(J\)) are expressed in Herts (Hz). Electrospray mass spectra (ESI-MS) were measured on a VG ProSpec triple focusing mass spectrometer.
Synthesis of methyl 4-(10-hydroxydec-1-ynyl)benzoate S3.

A flask containing a mixture of methyl-4-iodobenzoate (S1) (850 mg, 3.2 mmol), CuI (62 mg, 0.32 mmol), and PdCl$_2$(PPh$_3$)$_2$ (114 mg, 0.16 mmol) in triethylamine (15 mL) was degassed via three freeze-pump-thaw cycles and placed under nitrogen. The reaction was heated at 60 °C for 30 minutes then 9-decyn-1-ol (S2) (500 mg, 3.2 mmol) was added dropwise. After 3 h, the product was collected as a yellow precipitate, which was further purified by flash chromatography (SiO$_2$, 1:4 ethyl acetate/hexanes) to afford methyl 4-(10-hydroxydec-1-ynyl)benzoate as a white solid (808 mg, 86% yield). M. p. 62.0 - 62.5 °C. $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta$ = 7.95 (d, $J = 8.8$ Hz, 2 H), 7.44 (d, $J = 8.8$ Hz, 2 H), 3.91 (s, 3 H), 3.65 (dt, $J = 5.3$, 7.1 Hz, 2 H), 2.43 (t, $J = 7.1$ Hz, 2 H), 1.64 – 1.58 (m, 4 H), 1.49 – 1.43 (m, 2 H), 1.40 – 1.32 (m, 6 H), 1.22 (t, $J = 5.3$ Hz, 1 H). $^{13}$C NMR (CDCl$_3$, 500 MHz, 298 K): $\delta$ = 166.7, 131.5, 129.4, 128.9, 128.8, 94.0, 80.1, 63.1, 52.2, 32.8, 29.3, 29.1, 28.8, 28.6, 25.7, 19.5. HR-MS (ESI) for C$_{18}$H$_{24}$O$_3$: [M]$^+$ calcd. 288.1725, found 288.1724.
Synthesis of methyl 4-(10-hydroxydecyl)benzoate S4.

4-(10-hydroxydec-1-ynyl)benzoate (440 mg, 1.5 mmol) was dissolved in methanol (15 mL) and purged with nitrogen. The Pd/C catalyst (10 wt %) was added and the flask was evacuated under vacuum and flushed with H₂ three times before leaving the reaction under a H₂ balloon at room temperature for 24 h. The mixture was filtered through packed celite, washed with more methanol and concentrated to dryness to give S4 (690 mg) as a pale yellow solid. M. p. 49.0 – 50.0 °C. ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 7.95 (d, J = 8.5 Hz, 2 H), 7.24 (d, J = 8.5 Hz, 2 H), 3.90 (s, 3 H), 3.64 (dt, J = 5.3 Hz, 7.9 Hz, 2 H), 2.65 (t, J = 7.9 Hz, 2 H), 1.63 – 1.53 (m, 4 H), 1.31 – 1.28 (m, 12 H), 1.22 (t, J = 5.4 Hz, 1H). ¹³C NMR (CDCl₃, 500 MHz, 298 K): δ = 167.2, 148.5, 129.6, 128.4, 127.6, 63.1, 52.0, 36.0, 32.8, 31.1, 29.5, 29.5, 29.4, 29.4, 29.2, 25.7. HR-MS (ESI) for C₁₈H₂₈O₃: [M]⁺ calcd. 292.2038, found 292.2041.

Synthesis of methyl 4-(10-bromodecyl)benzoate S5.

A flask containing S4 (100 mg, 0.34 mmol) and PPh₃ (96 mg, 0.37 mmol) in CH₂Cl₂ (6 mL) was degassed and cooled to 0 °C. After 10 minutes, N-bromosuccinimide (61 mg, 0.34 mmol) was added and the reaction was allowed to warm to room temperature for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO₂, ethyl acetate/hexanes) to afford methyl S5 as a white solid (90 mg, 74 % yield). ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 7.95 (d, J = 8.5 Hz, 2 H), 7.23 (d, J = 8.5 Hz, 2 H), 3.89 (s, 3 H), 3.40 (t, J = 6.9 Hz, 2 H), 2.64 (t, J = 7.8 Hz, 2 H), 1.84 (dt, J = 6.9 Hz, 6.9 Hz, 2 H), 1.64 – 1.58 (m, 2 H), 1.43-1.37 (m, 2 H), 1.30 – 1.27 (m, 10 H).

Synthesis of methyl 4-(10-(acetylthio)decyl)benzoate S6.

A flask containing S5 (100 mg, 0.28 mmol) and potassium thioacetate (32 mg, 0.28 mmol) in DMF (6 mL) was stirred at room temperature and left for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO₂, 1:4 ethyl acetate/hexanes) to afford methyl S6 as clear oil (74 mg, 76 % yield). ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 7.95 (d, J =
8.5 Hz, 2 H), 7.24 (d, J = 8.5 Hz, 2 H), 3.90 (s, 3 H), 2.86 (t, J = 7.3 Hz, 2 H), 2.65 (t, J = 7.8 Hz, 2 H), 2.32 (s, 3 H), 1.66 – 1.52 (m, 4 H), 1.38 – 1.26 (m, 12 H).

**Synthesis of 4-(10-(mercaptodecyl)benzoic acid (p-MDBA).**

S6 (263 mg, 0.75 mmol) was dissolved in 10 % sodium hydroxide (4 mL) and refluxed at 130 °C until the reaction was complete in ~1.5 h. The mixture was cooled and acidified quickly to pH 3. The solid was collected by filtration, rinsed with water, and then purified by flash chromatography (SiO₂, 1:9 MeOH/CH₂Cl₂) to afford p-MDBA as a white solid (161 mg, 73 % yield). M.p. 118.0 °C; HR-MS (ESI) for C₁₇H₂₆O₂S: [M–H]⁺ calcd. 293.1581, found 293.1580; ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 8.01 (d, J = 8.5 Hz, 2 H), 7.28 (d, J = 8.5 Hz, 2 H), 2.67 (t, J = 7.6 Hz, 2 H), 2.52 (pseudo dt, J = 7.6 Hz, 7.6 Hz, 2 H), 1.66 – 1.57 (m, 4 H), 1.40 – 1.27 (m, 13 H). ¹³C NMR (CDCl₃, 500 MHz, 298 K): δ = 172.1, 149.6, 130.3, 128.6, 126.7, 36.11, 34.1, 31.1, 29.5 (2C), 29.4, 29.2, 29.1, 28.4, 24.7.

![Scheme 2: Preparation of m-MDBA](image)
Synthesis of ethyl 3-(10-hydroxydec-1-ynyl)benzoate S8.

A flask containing a mixture of ethyl 3-iodobenzoate (S7) (2.0 g, 7.2 mmol), CuI (138 mg, 0.72 mmol), and PdCl$_2$(PPh$_3$)$_2$ (254 mg, 0.36 mmol) in triethylamine (36 mL) was degassed via three freeze-pump-thaw cycles and placed under nitrogen. The reaction was heated at 60 °C for 30 minutes then 9-decyn-1-ol (S2) (1.1 g, 7.2 mmol) was added dropwise. After 2 h, the reaction mixture was concentrated, and the residue was purified by flash chromatography (SiO$_2$, 1:4 ethyl acetate/hexanes) to afford S8 as orange oil (1.87g, 85 % yield). $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 8.07$ (t, $J = 1.5$ Hz, 1 H), 7.94 (dt, $J = 1.5$ Hz, 7.7 Hz, 1 H), 7.56 (dt, $J = 1.5$ Hz, 7.7 Hz, 1 H), 7.36 (t, $J = 7.7$ Hz, 1 H), 4.37 (q, $J = 7.1$ Hz, 2 H), 3.65 (br t, $J = 5.0$ Hz, 2 H), 2.41 (t, $J = 7.1$ Hz, 2 H), 1.64 – 1.55 (m, 4 H), 1.49 – 1.30 (m, 12 H).

Synthesis of ethyl 3-(10-hydroxydecyl)benzoate S9.

S8 (1.9 g, 6.2 mmol) was dissolved in methanol (30 mL) and purged with nitrogen. The Pd/C catalyst (10 wt %) was added and the flask was evacuated under vacuum and flushed with H$_2$ three times before leaving the reaction under a H$_2$ balloon at room temperature for 24 h. The mixture was filtered through packed celite, washed with more methanol, and concentrated to dryness to give S9 (1.7 g, 91%) as an orange oil which was used without further purification. $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 7.86$ – 7.85 (m, 2 H), 7.38 – 7.32 (m, 2 H), 4.38 (q, $J = 7.1$ Hz, 2 H), 3.63 (broad t, $J = 6.0$ Hz, 2 H), 2.65 (t, $J = 7.7$ Hz, 2 H), 1.65 – 1.54 (m, 4 H), 1.41 – 1.28 (m, 16 H).

Synthesis of ethyl 3-(10-bromodecyl)benzoate S10.

A flask containing S9 (1.7 g, 5.6 mmol) and PPh$_3$ (1.6 g, 6.0 mmol) in CH$_2$Cl$_2$ (90 mL) was cooled to 0 °C. After 10 minutes, N-bromosuccinimide (1.0 g, 5.6 mmol) was added and the reaction was allowed to warm to room temperature and left for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO$_2$, 1:4 ethyl acetate/hexanes) to afford S10 as clear oil (1.79 g, 86 % yield). $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 7.86$ (br s, 2 H),
7.38 – 7.31 (m, 2 H), 4.38 (q, J = 7.1 Hz, 2 H), 3.41 (t, J = 7.0 Hz, 2 H), 2.65 (t, J = 7.7 Hz, 2 H), 1.85 (q, J = 7.3 Hz, 2 H), 1.62 (br t, J = 6.5 Hz, 2 H), 1.45 – 1.37 (m, 5 H), 1.37 – 1.24 (m, 10 H). $^{13}$C NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 166.9, 143.1, 132.9, 130.4, 129.5, 128.2, 126.9, 60.9, 35.7, 34.1, 32.8, 31.4, 29.4, 29.4, 29.2, 28.7, 28.2, 14.4$. HR-MS (ESI) for C$_{19}$H$_{29}$BrO$_2$: [M]$^+$ calcd. 370.1330, found 370.1331.

**Synthesis of ethyl 3-(10-(acetylthio)decyl)benzoate S11.**

A flask containing S10 (1.7 g, 4.6 mmol) and potassium thioacetate (0.58 g, 5.1 mmol) in DMF (92 mL) was stirred at room temperature for 5 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO$_2$, 1:4 ethyl acetate/hexanes) to afford S11 as pale yellow oil (1.58 g, 94 %). $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 7.86$ (br s, 2 H), 7.37 – 7.32 (m, 2 H), 4.38 (q, J = 7.2 Hz, 2 H), 2.86 (t, J = 7.3 Hz, 2 H), 2.65 (t, J = 7.7 Hz, 2 H), 2.32 (s, 3 H), 1.64 – 1.53 (m, 4 H), 1.41-1.26 (m, 15 H). $^{13}$C NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 196.1, 166.9, 143.2, 133.0, 129.5, 128.2, 126.9, 60.9, 35.8, 34.0, 31.4, 30.7, 29.5, 29.5, 29.4, 29.2, 29.1, 28.8, 24.7, 14.4$. HR-MS (ESI) for C$_{21}$H$_{32}$O$_3$S: [M+H]$^+$ calcd. 365.2150, found 365.2152.

**Synthesis of 3-(10-(mercaptodecyl)benzoic acid (m-MDBA).**

A flask containing S11 (500 mg, 1.4 mmol) was dissolved in 10 % sodium hydroxide (8 mL) and refluxed at 130 °C until the reaction was complete in ~5.5 h. The mixture was cooled and acidified quickly to pH 2-3. The solid was collected by filtration and washed with water, then purified by flash chromatography (SiO$_2$, 1:9 MeOH/CH$_2$Cl$_2$) to afford m-MDBA as a white solid (226 mg, 56 % yield). M.p. 76.1 – 76.3 °C; HR-MS (ESI) for C$_{17}$H$_{26}$O$_2$S: [M–H]$^-$ calcd. 293.1570, found 293.1568; $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 7.94$ (br s, 2 H), 7.44 – 7.37 (m, 2 H), 2.67 (t, J = 7.6 Hz, 2H), 2.52 (q, J = 7.3 Hz, 2 H), 1.65 – 1.59 (m, 4 H), 1.37-1.27 (m, 13 H); $^{13}$C NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 172.4, 143.4, 134.0, 130.1, 129.2, 128.4, 127.6, 35.7, 34.1, 31.4, 29.5 (2 C), 29.4, 29.2, 29.1, 28.4, 24.7.

A flask containing a mixture of dimethyl-5-iodoisophthalate (S12) (2.0 g, 6.2 mmol), CuI (119 mg, 0.62 mmol), and PdCl₂(PPh₃)₂ (219 mg, 0.31 mmol) in triethylamine (36 mL) was degassed via three freeze-pump-thaw cycles and placed under nitrogen. The reaction was heated at 60 °C for 30 minutes then 9-decyn-1-ol (S2) (964 mg, 6.2 mmol) was added dropwise. After 2 h, the reaction mixture was concentrated, and the residue was purified by flash chromatography (SiO₂, 1:4 ethyl acetate/hexanes) to afford S13 as a white solid (1.83 g, 85 % yield). ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 8.55 (t, J = 1.8 Hz, 1 H), 8.22 (d, J = 1.8 Hz, 2 H), 3.95 (s, 6 H), 3.65 (dt, J = 5.2 Hz, 7.0 Hz, 2 H), 2.42 (t, J = 7.0 Hz, 2 H), 1.64 – 1.58 (m, 4 H), 1.49 – 1.44 (m, 2 H), 1.40 – 1.35 (m, 6 H), 1.29 (t, J = 5.4 Hz, 1 H). ¹³C NMR (CDCl₃, 500 MHz, 298 K): δ = 166.5, 143.8, 133.9, 130.5, 128.2, 63.1, 52.3, 35.6, 32.8, 31.2, 29.5, 29.4, 29.4, 29.4, 29.1, 25.7.

Scheme 3: Preparation of bm-MDBA
Synthesis of dimethyl 5-(10-hydroxydecyl)isophthalate S14.

S13 (1.8 g, 5.3 mmol) was dissolved in methanol (40 mL) and purged with nitrogen. The Pd/C catalyst (10 wt %) was added, the flask was evacuated under vacuum and flushed with H₂ three times before leaving the reaction under a H₂ balloon at room temperature for 24 h. The mixture was filtered through packed celite, washed with more methanol, and then concentrated to dryness to give S14 (1.80 g, 98% yield) as an orange solid. ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 8.52 (t, J = 1.7 Hz, 1 H), 8.22 (d, J = 1.7 Hz, 2 H), 3.94 (s, 6 H), 3.61 (t, J = 6.7 Hz, 2 H), 2.70 (t, J = 7.7 Hz, 2 H), 1.67 – 1.61 (m, 2 H), 1.57 – 1.53 (m, 2 H), 1.31 – 1.28 (m, 13 H). MS (EI) for C₂₀H₃₀O₅: [M+Na]⁺ calcd. 373.20, found 373.20.

Synthesis of dimethyl 5-(10-bromodecyl)isophthalate S15.

A flask containing S14 (1.8 g, 5.1 mmol), and PPh₃ (1.4 g, 5.5 mmol) in CH₂Cl₂ (85 mL) was cooled to 0 °C. After 10 minutes, N-bromosuccinimide (909 mg, 5.1 mmol) was added and the reaction was allowed to warm to room temperature and left for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (SiO₂, 1:4 ethyl acetate/hexanes) to afford S15 as clear oil (1.75 g, 83% yield). ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 8.50 (t, J = 1.6 Hz, 1 H), 8.05 (d, J = 1.6 Hz, 2 H), 3.94 (s, 6 H), 3.41 (t, J = 7.0 Hz, 2 H), 2.70 (t, J = 7.8 Hz, 2 H), 1.85 (dt, J = 7.0 Hz, 7.8 Hz, 2 H), 1.68 – 1.61 (m, 2 H), 1.43 – 1.38 (m, 2 H), 1.30 – 1.28 (m, 10 H). ¹³C NMR (CDCl₃, 500 MHz, 298 K): δ = 166.5, 143.8, 133.9, 130.5, 128.2, 52.3, 35.6, 34.1, 32.8, 31.2, 29.4, 29.4, 29.1, 28.7, 28.2. HR-MS (ESI) for C₂₀H₂₉BrO₄: [M⁺]⁺ calcd., 414.1229, found 414.1229.

Synthesis of dimethyl 5-(10-(acetylthio)decyl)isophthalate S16.

A flask containing S15 (1.7 g, 4.0 mmol) and potassium thioacetate (514 mg, 4.5 mmol) in DMF (80 mL) was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (SiO₂, 1:4 ethyl acetate/hexanes) to afford S16 as a white solid (1.51 g, 90 % yield). M. p. 71.0 – 72.0 °C. ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 8.50 (s, 1 H), 8.05 (s, 2 H), 3.94 (s, 6 H), 2.85 (t, J = 7.3 Hz, 2 H), 2.69 (t, J = 7.5 Hz, 2 H), 2.32 (s, 3 H),
1.65 – 1.64 (m, 2 H), 1.56 – 1.54 (m, 2 H), 1.30 – 1.26 (m, 12 H). $^{13}$C NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 196.1, 166.5, 143.8, 133.9, 130.5, 128.2, 52.3, 35.6, 31.2, 30.7, 29.5, 29.4, 29.4, 29.2, 29.1, 28.8.

HR-MS (ESI) for C$_{22}$H$_{32}$O$_5$S: [M]$^+$ calcd. 408.1970, found 408.1970.

**Synthesis of 5-(10-(mercaptodecyl))isophthalic acid (bm-MDBA).**

A flask containing S16 (400 mg, 0.98 mmol) was dissolved in 10 % sodium hydroxide (6 mL) and refluxed at 130 °C until the reaction was complete in 3 h. The mixture was cooled and acidified quickly to pH 2. The solid was collected by filtration and washed with water, then purified by flash chromatography (SiO$_2$, 1:9 MeOH/CH$_2$Cl$_2$) to afford bm-MDBA as a white solid (216 mg, 65 % yield). M.p. 204.5 – 205.0 °C; HR-MS (ESI) for C$_{18}$H$_{26}$O$_4$S: [M–H]$^-$ calcd. 337.1468, found 337.1467; $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 13.20$ (broad s, 2), 8.61 (s, 1 H), 7.95 (s, 2 H), 2.67 (t, $J = 7.3$ Hz, 2 H), 2.56 (pseudo dt, $J = 7.3$ Hz, 7.3 Hz, 2 H), 1.44 – 1.37 (m, 4 H), 1.36 – 1.34 (m, 13 H); $^{13}$C NMR (CDCl$_3$, 500 MHz, 298 K): $\delta = 171.6, 134.5, 134.4, 130.0, 129.6, 35.6, 34.1, 31.2, 29.6, 29.6, 29.5, 29.4, 29.2, 26.4, 24.7.
2. CONTACT ANGLE DATA & ANALYSIS

Figure S1 displays characteristic and representative images of water droplets on the surface of each type of ‘as prepared’ MDBA SAM on Au(111) substrates. It is evident from inspection that the static contact angles for the p-MDBA (figure S1(a)) and bm-MDBA (figure S1(c)) SAMs are similar and very shallow, which is indicative of a hydrophilic surface. In contrast, the contact angle of 58° for the m-MDBA SAM (figure S1(b)) is much larger, thereby demonstrating the more hydrophobic behavior one would anticipate if the carboxyl groups were partially buried within the monolayer.

Figure S1: Characteristic static contact angle images with water for ‘as prepared’ SAMs of (a) p-MDBA, (b) m-MDBA and (c) bm-MDBA
3. X-RAY ABSORPTION SPECTROSCOPY (XAS) DATA & ANALYSIS

3.1 Instrumentation & Methods

X-ray absorption spectra were recorded on VUV BL8.2 of the Stanford Synchrotron Radiation Laboratory (SSRL, SPEARIII) at the Stanford Linear Accelerator (SLAC). BL8.2 is served by a bending magnet and a spherical grating monochromator and offers an energy resolution of ~0.2eV for XAS experiments conducted at the carbon K-edge. The cross-section of the focused beam was ~1 mm in diameter at the sample surface. XAS spectra were recorded simultaneously in the total electron yield (TEY) mode by measuring the total current leaving the experimental sample as the X-ray energy was scanned across the absorption edge. The AEY signal was provided by measuring the intensity of the appropriate Auger electron during the course of each scan. All XAS signals were normalized to the $I_0$ current, which was recorded for the incident X-ray beam via a Au grid located upstream of the experimental sample. To ensure minimal effect on the $I_0$ signal from, predominantly organic, contaminants absorbed on the surface of the grid, it was frequently coated with a fresh layer of evaporated Au. All XAS measurements were conducted at base pressures $\leq 1 \times 10^{-9}$ Torr. The degree of linear polarization, $P$, in the incident beam was determined prior to each series of X-ray absorption experiments via carbon K-edge XAS measurements of highly oriented pyrolytic graphite (HOPG). XAS spectra were recorded at a series of angles of incidence between a freshly cleaved sample of HOPG and the X-ray beam. The axes through which the HOPG was rotated were carefully selected such that comparison of the C(1s) $\pi^*$ resonance intensity in the XAS spectra yielded the relative magnitudes of $E_p^2$ and $E_s^2$, where $E_p$ and $E_s$ represent the electric field in-plane and perpendicular to the plane of incidence, respectively. $P$ was then calculated according to $^{2,3}$:

$$P = \frac{E_p^2}{E_s^2 + E_p^2}$$

The calculated polarization was 99% in the plane of the storage ring during the course of the experiments presented in this manuscript. For carbon XAS measurements, the energy scale on BL8.2 was calibrated to the $\pi^*$ resonance for HOPG, for which the energy was assigned to be 285.38 eV$^4$. Care
was taken to ensure that the effects of beam damage on the MBA SAM samples were minimized when conducting XAS measurements. Each spectrum was recorded from a fresh region of the sample surface and beam exposure during data collection was limited to the time frame required for good signal-to-noise statistics. For carbon K-edge XAS, which was collected over a spectral range of 280-325 eV, this corresponded to ~ 5 min per spectrum.

3.2 Protocols for Analysis of XAS Data

XAS yields a quantitative assignment of bond orientation through analysis of the polarization dependencies of various resonances. Hence, the technique can be used to determine the orientation of the aromatic ring and carboxyl group contained within the MDBA SAMs. The intensity of an XAS resonance is proportional to the dot product of the electric field vector in the X-ray beam and the transition dipole moment for the unoccupied orbital. For the MDBA SAMs, Au(111) has three-fold azimuthal symmetry. The transition dipole moment can be modeled as a vector for the π* orbital that extends throughout the aryl and carboxyl groups of each MDBA isomer and lies perpendicular to the plane of the molecule. For resonances modeled by a vector transition dipole moment, the intensity, \( I_v \), is expressed as:

\[
I_v(\theta, \alpha) \propto \frac{1}{3} P \left[ 1 + \frac{1}{2} (3\cos^2 \alpha - 1)(3\cos^2 \theta - 1) \right] + \frac{1}{2} (1 - P) \sin^2 \alpha
\]

where \( \theta \) represents the angle between the incident radiation and the surface (≤ 90°) and \( \alpha \) represents the angle between the transition dipole moment vector (TDMV) and the surface normal. It is noted that there is a substantial separation in energy between the π* resonances for the aryl and carboxyl carbon atoms due to the electron withdrawing effect of the oxygen atoms on the carboxyl carbon. As a consequence, these resonances are clearly resolved from one another in spectra collected on BL8.2. For the C-C and C-O \( \sigma^* \) and the Rydberg (\( R^* \))/C-H \( \sigma^* \) resonances, the transition dipole moment is modeled by a plane, which is co-incident with the plane of the aryl ring in the isomers of MDBA. In this instance, the resonance intensity \( I_p \) is expressed as:

\[
I_p(\theta, \alpha) \propto \frac{1}{3} P \left[ 1 + \frac{1}{2} (3\cos^2 \alpha - 1)(3\cos^2 \theta - 1) \right] + \frac{1}{2} (1 - P) \sin^2 \alpha
\]
where $\gamma$ represents the angle between the surface normal and the normal to the plane of the transition dipole moment. To remove the proportionality, ratios are taken between spectra recorded at different angles of incidence. In order to simplify analysis, the intensities are left as functions of cosine squared.

With $\Theta = \cos^2 \theta$, $A = \cos^2 \alpha$ and $\Gamma = \cos^2 \gamma$ the intensities from eqs. 1 and 2 become:

$$
\frac{I_p(\theta,A)}{I_p(\theta,A)} = \frac{P(3A-1)\theta_i-A+1}{P(3A-1)\theta_j-A+1}
$$

and

$$
\frac{I_p(\theta_i,\Gamma)}{I_p(\theta_j,\Gamma)} = \frac{P(3\Gamma-1)\theta_i-\Gamma-1}{P(3\Gamma-1)\theta_j-\Gamma-1}
$$

respectively. These two equations are linear in $\Theta_i$. A linear regression is obtained from all spectra acquired at $\Theta_i$ versus all spectra acquired at $\Theta_j$, which allows $\alpha$ and $\gamma$ to be solved as a function of the slopes or offsets. In principle, a high degree of precision, $< \pm 1^\circ$, is possible from regression analysis on spectra recorded at multiple angles of incidence. Nevertheless, several additional sources of systematic error are omitted from this estimate and the predicted accuracy is actually between $\pm 4-5^\circ$.

As discussed briefly in the full paper, one cannot treat the tilt (colatitudinal) and twist (dihedral) angles of the MDBA aromatic endgroups independently when using the XAS $\pi^*$-resonance intensities to obtain orientational information. This restriction is imposed because identification of the tilt and twist angles requires that one deconvolve two degrees of freedom and analysis of the XAS spectra provides only one. Nonetheless, the application of a well-defined protocol enables the assignment of a limited series of tilt/twist combinations that are both (1) consistent with the XAS data and (2) physically viable. The protocol applied during this study is summarized as follows:

(i) Theoretical transition dipole moment vectors (TDMVs) are calculated for every possible tilt/twist combination that could be adopted by the aromatic endgroup (i.e. the aryl ring and carboxyl group(s)) of the MBDA isomer using the “building block” approach.

(ii) Theoretical XAS intensities from all possible molecular/moiety orientations are compared with those obtained from linear regression analysis of the experimental XAS data. Close agreement
between the theoretical and experimental XAS indicates potential tilt/twist combinations for the aromatic endgroups within the SAM sample.

(iii) The subset of orientations obtained via comparison of the theoretical and experimental treatment is evaluated for physical viability via steric considerations. For studying the MDBA SAMs, the ends of the alkyl chains, defined by the uppermost carbon atom in each chain, are treated as a rigid plane whose surface is parallel to the Au(111) substrate surface (figure S2). Any configuration in which the aromatic endgroup of the MDBA (i.e. the aryl ring or carboxyl group(s)) break this plane is then considered to be sterically forbidden because the aromatic endgroup would be directed into the alkyl framework of the SAM, which, in the vast majority of cases, is not physically viable. The tilt/twist combinations obtained from the experimental XAS are then compared with the sterically permissible configurations to identify the manifold of possible orientations for the aromatic endgroup. Note that this analysis assumes that the terminal carbons of the alkyl chains are all equidistant from the Au(111) surface, which could induce a small degree of error.

The number of orientations identified using this protocol is often limited for any given sample (as illustrated later in this document) and, therefore, offers valuable insight into the structure of the SAM at various stages of the crystallization process.

For the purposes of clarity and direct comparison between MDBA samples exposed to different treatments, the viable orientations obtained identified for each set of XAS data is displayed graphically (referred to as ‘tilt/twist’ plots throughout this supporting information document). In each graph, the y-axis corresponds to the colatitudal (tilt) angle, for which 0° corresponds to a configuration in which the transition dipole moment vector of the π*-orbital lies parallel to the Au(111) substrate surface when the C-C σ-bond between the aryl ring and alkyl chain of the MDBA molecule is directed away from the substrate along the Au(111) surface normal. Conversely, a tilt angle of 180° also represents a configuration in which the transition dipole moment of the π*-orbital is parallel to the substrate, but the
C-C σ-bond between the aryl ring and alkyl chain is directed into the Au(111) along the surface normal. The x-axis corresponds to the dihedral (twist) angle represents the degree of rotation about an axis coincident with the C-C σ-bond between the aryl ring and alkyl group. At a tilt angle of 90° and a twist angle of 0 (and 360) or 180°, the plane of the MBA molecules is parallel to the plane of the Au(111) substrate surface.

The white region of each plot corresponds to molecular orientations that are sterically forbidden. For example, any orientation in which the tilt angle is > 90° is forbidden because the C-C σ-bond between the aryl ring and alkyl chain would break the plane formed by the carbon atoms at the end of the alkyl chains. By way of contrast, the grey region corresponds to the sterically permissible orientations.

Figure S2: Schematic to illustrate location of the plane formed by carbon atoms at the end of the alkyl chain in SAMs prepared from MDBA molecules on Au(111) substrates. This plane is indicated by the dashed red line and labeled by the letter (a). Importantly, it lies parallel to the Au(111) surface. Note that the schematic contains p-MDBA molecules of arbitrary orientation – the arrangement of the molecules is not necessarily intended to reflect the orientation and/or structure of the p-MDBA SAMs at any stage of the crystallization process, including their 2D packing on the Au(111) surface. Moreover, an equivalent plane can be constructed for the m- and bm-MDBA SAMs.
orientations of the MDBA molecules. The red annulus on each plot corresponds to the combinations of twist and tilt angles obtained from analysis of the experimental carbon K-edge XAS data. Significantly, the sterically forbidden combinations are identified as the portion of this red annulus that superimposes the white region of each plot. Conversely, the sterically allowed combinations superimpose the grey region of the graph. The thickness of the red annulus corresponds to one standard deviation over all six of the slopes obtained from equation 3 when dividing through each of the angles of incidence between the axis of the x-ray beam and the sample surface. As such, it provides a useful indication of one source of experimental error (but, importantly, not all sources) in each set of XAS data. An additional (blue) annulus is also included on each of the plots as a guide for the eye. This blue annulus corresponds to a system in which the TDMV of the aromatic endgroup resides exactly at the magic angle (54.7°) or, alternatively, a system in which the aromatic endgroups exhibit a random distribution of orientations. Note that the tilt angle of the aromatic endgroup at zero twist for the tilt/twist plots will be equal to 90°±(TDM angle)°.

Throughout the main manuscript and this Supporting Information document, it is evident that we only conduct linear regression analysis on the π*-resonance of the aryl ring and not on the π*-resonance of the carboxyl groups or the σ*-resonances observed at higher energy. The choice to focus on the aryl π*-resonance rather than the carboxyl π*-resonance is rationalized by the lower error associated with linear regression analysis of an isolated resonance versus one that it convolved with other peaks, as discussed in the main manuscript. Meanwhile, the structure of the MDBA molecules prevents linear regression analysis of the σ* resonance intensities. This limitation arises due to the fact that C-C bonds from both the aromatic headgroup and the alkyl chain contribute to the C-C σ* signal, which necessitates that one deconvolve four degrees of freedom (the tilt and twist angles of the C-C bonds in both the alkyl and aromatic groups) when analysis of the XAS data offers only the ability to determine one degree of freedom or the interdependence of two. Nonetheless, it should be noted that the difference spectra for all of the MBDA SAMs display angular dependence in the σ* resonances, irrespective of their treatment (i.e. ‘as prepared’ versus exposure to Ca²⁺-bearing solution or amorphous mineral precipitation).
We also note that, in some cases, the difference spectra for the MDBA SAMs supporting Mg-stabilized ACC contain strong $\pi^*$-features associated with the carbonate group of the mineral phase, which presents the possibility that the minerals exhibit some degree of order. Linear regression analysis of the carbonate $\pi^*$-resonances enables evaluation of the possibility of order within the mineral phase. In all cases, the TDMVs associated with the carbonate $\pi$-system reside within experimental error of the magic angle, which denotes one of two possibilities: (1) the carbonate groups exhibit statistically averaged disorder or (2) the mineral has a preferred orientation in which the TDMV of the carbonate groups is close to the magic angle. Although one cannot definitively distinguish between (1) and (2) based upon analysis of the XAS intensities alone, a consideration of the experimental system under investigation and comparison with complementary data from alternative techniques indicates that (1) is more probable than (2). In particular, the high concentration of Mg$^{2+}$ within the growth solution is anticipated to stabilize an amorphous mineral phase, which would be consistent with (1). Meanwhile, SEM micrographs of the mineral phase (see Section 4) reveal that the Mg$^{2+}$-stabilized particles are rounded, which is a common feature of amorphous minerals. In either event, the apparent strength of the carbonate $\pi^*$ difference features are somewhat misleading because they are tempered by the high intensities of the carbonate $\pi^*$-resonances in the raw XAS data – i.e. the differences between the resonance intensities observed in the difference spectra are small with respect to the resonance intensities themselves.

3.3 XAS Data for p-MDBA SAMs

Figure S3 displays the carbon K-edge XAS spectra for three distinct ‘as prepared’ p-MDBA SAMs on Au(111) substrates and each data set is accompanied by the corresponding tilt/twist plot obtained via linear regression analysis. This series of data includes the upper (figure S3(a-b)) and lower (figure S3(c-d, e-f)) bounds of tilt angles obtained for the aromatic endgroups within the series of ‘as prepared’ p-MDBA SAMs studied in this work. Inspection of the $\pi^*$-signals in the difference spectra of figures S3(a), (c) and (e) make for an interesting comparison: the $\pi^*$ difference features are directed upwards for the first SAM (figure S3(a)), which indicates that the TDM vector for the aromatic endgroup is tilted by more than 54.7° (the magic angle). In contrast, the $\pi^*$ difference features for the second and third
samples (figures S3(c) and S3(e) respectively) are directed downwards, corresponding to a TDM vector that has an angle less than 54.7°. This behavior is reflected in the tilt/twist plots, in which the red annulus of the experimental XAS data lies outside of the blue annulus for the first sample (figure S3(b)) and inside for the second and third (figure S3(d) and (f)) samples. A more significant feature of the data, however, is that the red annuli obtained from analysis of the three sets of the XAS data are all within experimental error of the blue annulus and one another. As a consequence, one can draw two important conclusions regarding the ‘as prepared’ p-MDBA SAMs: (1) the p-MDBA SAMs consistently and reproducibly adopt a surface structure containing a defined array of endgroup orientations but (2) it is not possible via linear regression analysis of the XAS to determine whether this array consists of endgroups with a well-defined orientation that yields a TDM vector close to the magic angle or a random distribution (i.e. statistically averaged disorder) of endgroups (as discussed in the full paper).
In the event that the aromatic endgroups within the p-MDBA SAMs exhibit well-defined carbon K-edge XAS data recorded for three distinct ‘as prepared’ p-MDBA SAMs on Au(111). (b), (d) and (f) display the corresponding tilt/twist plots for the aromatic endgroup in each sample. Labels I through IV correspond to those in the full paper.

**Figure S3:** (a), (c) and (e) display carbon K-edge XAS data recorded for three distinct ‘as prepared’ p-MDBA SAMs on Au(111). (b), (d) and (f) display the corresponding tilt/twist plots for the aromatic endgroup in each sample. Labels I through IV correspond to those in the full paper.
orientations rather than statistically averaged disorder, further inspection of figures S3(b, d and f) provides additional information regarding the monolayer composition and structure. Evaluation of the XAS data via linear regression analysis and accounting for steric effects yields an extremely small subset of physically viable combinations of tilt and twist angles for the aromatic endgroups. The potential tilt angles within this subset are limited to a range of less than 20° (closer to 15° for some samples) encompassing approximately $35^\circ < \theta < 55^\circ$ with accompanying twist angles from similarly restricted ranges (approximately $135^\circ < \varphi < 225^\circ$ and $315^\circ < \varphi < 45^\circ$). In all of the physically viable combinations of tilt and twist, the carboxyl group will be accessible at the surface of the p-MDBA SAM, which correlates with the hydrophilic character of the monolayer surface revealed via static contact angle measurements with water. We note that the carboxyl groups could also be accessible at the surface of a p-MDBA SAM composed of molecules with statistically averaged disorder among the aromatic endgroups, thereby leading to the hydrophilic character of the p-MDBA SAMs.

**Figure S4:** (a) Characteristic, normalized carbon $K$-edge XAS data recorded for a p-MDBA SAM after immersion in Ca$^{2+}$-bearing solution for 20 min (as displayed in the full paper) and (b) the corresponding tilt/twist plot for the XAS data.
Profound differences are observed in the carbon K-edge XAS data (as discussed in the full paper) and accompanying tilt/twist plots following exposure of the p-MDBA SAMs to Ca\(^{2+}\)-bearing solution (figure S4) and the precipitation of Mg-stabilized ACC (figure S5). The more pronounced \(\pi^*\)-features in the difference spectra (figures S4(a) and S5(a)) with respect to the ‘as prepared’ sample (figures S3(a, c and e)) result in considerable changes to the appearance of the tilt/twist plots: the red annulus of tilt/twist combinations derived from the experimental XAS resides much further outside of the blue reference annulus in figures S4(b) and S5(b) than in figure S3(b, d and f). In fact, the difference in the XAS-derived and physically viable manifold of tilt/twist angles for the ‘as prepared’ p-MDBA SAMs with respect to those exposed to Ca\(^{2+}\)-bearing solution or Mg-stabilized ACC precipitation reside well beyond experimental error. It is important to note that although the manifolds of viable orientations for the ‘as prepared’ p-MDBA SAMs and those exposed to the growth solution/ACC formation share some of the same tilt and twist angles, they do not share any of the same combinations of tilt/twist angles.

Figure S5: (a) Characteristic, normalized carbon K-edge XAS data recorded for a p-MDBA SAM on Au(111) after precipitation of an Mg-stabilized ACC layer onto its surface (as displayed in the full paper) and (b) the corresponding tilt/twist plot for the XAS data. V denotes the \(\pi^*\) resonance associated with the carbonate ion of the Mg-ACC.
This feature of the data demonstrates that the aromatic endgroups reorient themselves within the growth solution for a SAM/mineral system that exhibits preferential ordering within the final suite of crystals (i.e., ‘templating’). When combined with the limited range of tilt angles exhibited by any of the samples, the mutually exclusive manifolds of endgroup orientations also validates using the tilt angle at a specific twist angle (selected to be 0° within the full paper) as a simple means of directly comparing the endgroup orientations within MDBA monolayers exposed to different conditions.

The manifolds of viable tilt/twist combinations for the p-MDBA SAMs immersed in Ca$^{2+}$-bearing solution and exposed to the precipitation of amorphous mineral are identical to within experimental error, as one would anticipate from the closely comparable aryl π* difference intensities observed in the experimental XAS. Each possible combination of tilt and twist within these manifolds lies beyond experimental error from the theoretical annulus derived for a disordered system and, as such, the p-MDBA SAMs exhibit well-defined endgroup orientations following exposure to the growth solution or, indeed, precipitation of the Mg-stabilized ACC. The range of XAS-derived and physically viable tilt angles slightly exceeds the extent observed for the ‘as prepared’ p-MDBA monolayers, encompassing approximately $22^\circ < \theta < 47^\circ$, while the accompanying twist angles also encompass a slightly wider scope and fall within $120^\circ < \varphi < 240^\circ$ and $300^\circ < \varphi < 60^\circ$. Even so, the manifold of viable tilt/twist combinations remains an extremely small subset of all possible configurations and provides an excellent indication of the endgroup orientation.

3.4 XAS Data for m-MDBA SAMs

Figure S6(a) displays representative carbon K-edge XAS spectra and associated difference signals obtained for the ‘as prepared’ m-MDBA SAMs on Au(111). The corresponding data for m-MDBA SAMs following exposure to Ca$^{2+}$-bearing solution and the formation of Mg-stabilized ACC is shown in figures S6(b) and (c) respectively. Comparison of the aryl π* difference signals provides an illustration that the orientation of the aromatic endgroups is the same, to within experimental error, in all three sample types, as described in the main manuscript. As a consequence, one can conclude that there is
minimal, if any, change in the orientation of these endgroups following immersion in the growth solution or exposure to precipitation of the Mg-incorporated mineral phase. This behavior, which contrasts so dramatically from the p-MDBA SAMs, is reflected in the tilt/twist plots displayed in figures S7 through S9 for the ‘as prepared’, ‘Ca$^{2+}$ solution treated’ and ‘exposed to Mg-ACC precipitation’ respectively: all three sample types exhibit comparable manifolds of viable orientations that are composed of very specific and limited combinations of tilt and twist angles. Importantly, each manifold resides beyond experimental error of the blue annulus, thereby confirming that the aromatic endgroups are not disordered and rather adopt well-defined (and statistically averaged) orientations. Characteristic tilt angles for the m-MDBA monolayers reside within the $24^\circ < \theta < 48^\circ$ range, while the associated twist angles fall between $123^\circ < \phi < 237^\circ$ and $303^\circ < \phi < 57^\circ$. 

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**Figure S6:** Normalized carbon K-edge XAS spectra recorded in the TEY mode for m-MDBA SAMs on Au(111): (a) ‘as prepared’, (b) following immersion in 10mM aqueous solution of Ca$^{2+}$ for 20 min and (c) after precipitation of an Mg-stabilized ACC layer. The horizontal dashed line running between the plots serve to aid in direct comparison between XAS spectra collected for the three m-MDBA samples.
These manifolds of viable tilt and twist angles observed for the m-MDBA monolayers in figures S7 through S9 are identical, to within experimental error, of the equivalent manifolds for p-MDBA SAMs that have been exposed to Ca$^{2+}$-bearing solution and the precipitation of Mg-stabilized ACC (figures S5 and S6 respectively). This feature of the data is anticipated based upon the similarity in the TDM vectors derived from the XAS spectra, yet reinforces an interesting feature of the MDBA SAM systems: despite such startling structural similarity in the monolayers after exposure to the growth solution (and mineral precipitation), the m-MDBA monolayers do not induce crystallization of calcite on preferred crystallographic planes, whereas calcite formed at the surface of p-MDBA SAMs exhibits a high degree of selectivity for nucleation on the (018) face. Therefore, it is evident that the presence of well-defined molecular orientation and 2D order within the MDBA SAMs alone is insufficient to yield ‘templating’ of the mineral – accessibility to the carboxyl functional group at the SAM surface and flexibility in the organic monolayer are both crucial components for obtaining preferential ordering among the final suite of calcite crystals.

**Figure S7:** (a) Characteristic, normalized carbon K-edge XAS data recorded for an ‘as prepared’ m-MDBA SAM on Au(111) and (b) the corresponding tilt/twist plot for the XAS data.
Figure S8: (a) Characteristic, normalized, carbon K-edge XAS data recorded for a m-MDBA SAM after immersion in Ca\(^{2+}\)-bearing solution for 20 min and (b) the corresponding tilt/twist plot for the XAS data.

Figure S9: (a) Characteristic, normalized carbon K-edge XAS data recorded for a m-MDBA SAM on Au(111) after precipitation of an Mg-stabilized ACC layer onto its surface and (b) the corresponding tilt/twist plot for the XAS data.
3.5 XAS Data for bm-MDBA SAMs

Figure S10 displays characteristic and normalized carbon $K$-edge XAS spectra and the associated tilt/twist plot for an ‘as prepared’ bm-MDBA SAM on Au(111). The corresponding data for bm-MDBA monolayers exposed to Ca$^{2+}$-bearing solution and the precipitation of Mg-stabilized ACC are displayed in figures S11 and S12 respectively. Inspection of the tilt/twist plots reveals comparable behavior to the m-MDBA monolayers. The manifold of tilt and twist angles for the aromatic endgroup remains unchanged, to within experimental error, after exposure of the ‘as prepared’ bm-MDBA SAMs to either the Ca$^{2+}$-bearing solution or precipitation of the amorphous mineral phase. Furthermore, each manifold resides beyond experimental error of the blue annulus, thereby indicating that the bm-MDBA SAMs are composed of molecules with statistically-averaged, well-defined orientations. It is also noteworthy that the manifolds for the m-MDBA and bm-MDBA monolayers are identical to within experimental error, as one would expect given the close similarities of the TDM vectors for their aromatic endgroups. The specific manifolds of tilt and twist angles determined for the bm-MBDA SAMs encompass the ranges $23^\circ < \theta < 47^\circ$ and $124^\circ < \varphi < 236^\circ$, $304^\circ < \varphi < 56^\circ$ respectively.

Figure S10: (a) Characteristic, normalized carbon $K$-edge XAS data recorded for an ‘as prepared’ bm-MDBA SAM on Au(111) (as displayed in the full paper) and (b) the corresponding tilt/twist plot for the XAS data.
The behavior of the bm-MDBA system demonstrates, once again, that an ordered monolayer composed of molecules with well-defined endgroup orientations does not necessarily yield nucleation of calcite on a specific plane. In addition, the availability of at least one carboxyl group at the surface of the bm-MDBA SAMs ensures
that the lack of a preferred crystallographic orientation among the crystals formed at the surface of the monolayer does not occur due to non-specific interactions, which could be the case for the m-MDBA SAMs.

3.6 Comparison of MDBA XAS Data with Endgroup Orientations of Molecules within SAMs of Similar Composition and Structure.

The main manuscript demonstrates that the aryl $\pi^*$ TDMV for all of the m- and bm-MDBA SAMs and also the p-MDBA SAMs after exposure to Ca$^{2+}$-bearing solution and mineral precipitation are within experimental error of the aryl $\pi^*$ TDMV for the aromatic endgroup in ‘even’ BP SAMs. Meanwhile, the methyl-terminated biphenyl endgroup of the BP molecules are reported to adopt an orientation with a tilt of 45° ($\pm$10°) and a twist of 61° ($\pm$10°). The orientation of the BP endgroups is extremely close to the tilt (~45°) and twist (~55° and its equivalents - 135°, 225° and 305°) angles that reside at the limits of the physically viable orientations of the m- and bm-MDBA SAMs and the p-MDBA SAMs after exposure to Ca$^{2+}$-bearing solution and mineral precipitation. Although not a definitive proof, such close similarity suggests that the isomers of MBDA and ‘even’ BP form SAMs with equivalent packing and molecular orientation, as one would anticipate given their comparable molecular structures. Figures S13(a) through (c) display schematics of the aromatic headgroups for the p-, bm- and m-MDBA SAMs respectively for orientations comparable to those adopted in the ‘even’ BP

![Figure S13: Skeletal diagrams for the aromatic endgroups of (a) p-MDBA, (b) bm-MDBA and (c) m-MDBA SAMs when oriented with a tilt angle, $\theta$, of ~45° and a twist angle, $\phi$, of ~55°. An accompanying diagram of a p-MDBA endgroup to indicate how the tilt and twist angles are defined and the orientation of the aryl $\pi^*$ TDMV with respect to the aryl ring is displayed in (d). Individual atoms are denoted by filled spheres with the following colors: carbon - grey, oxygen - red and hydrogen – white. The white dotted line displayed across (a) through (c) is a guide for the eye and represents a planar surface.](image-url)
SAMs, i.e. at the limit of the physically viable combinations of tilt and twist determined from analysis of the experimental XAS data (~45° tilt and ~55° twist). Figure S13(d) provides an accompanying illustration, reproduced from the main manuscript, that indicates how the tilt and twist angles are defined for the aromatic headgroup of the MDBA molecules and the orientation of the aryl π* TDMV.

Inspection and comparison of the schematics displayed in figures S13(a) through (c) supports and reinforces many of the conclusions drawn in the main manuscript:

(i) Figures S13(a) and (b) demonstrate that one carboxyl group of each bm-MDBA molecule is exposed at the surface of the respective SAMs, whereas the carboxyl group of the m-MDBA molecule is not. This is consistent with the hydrophilic behavior displayed in the contact angle measurements.

(ii) Figures 13(b) and (c) illustrate that both the bm- and m-MDBA molecules have a carboxyl group that would be directed into a monolayer structure. Within a densely packed SAM, these carboxyl groups will be inaccessible to water molecules, which explains the reduced hydrophilicity of the m-MDBA SAMs with respect to the p- and bm-MDBA SAMs. The inaccessibility of these buried carboxyl groups also prevents them from taking part in specific interactions with the nascent calcite crystals at the surface of the SAM. Significantly, the orientation of the buried carboxyl groups would not preclude the formation a SAM structure equivalent to the (5√3 x 3) arrangement adopted by ‘even’ BP SAMs on Au(111) nor, indeed, any closely related structure based upon a herringbone-like packing of the aromatic endgroups. Nonetheless, it will restrict, and potentially prevent, reorientation of the aromatic endgroup because any change in orientation of the carboxyl groups will bring about unfavorable steric interactions with neighboring molecules. The carboxyl groups have a large lateral, i.e. in-plane, component to their orientation which will cause them to extend into unoccupied spaces between adjacent headgroups within a herringbone-like arrangement. In this configuration, even small reorientations of the aromatic endgroup will be prevented by unfavorable electrostatic interactions with neighboring molecules. This is not the case for the p-MDBA molecules since their only carboxyl group is directed out the monolayer, thereby allowing greater freedom of movement in the aromatic endgroup before incurring any steric restrictions.

(iii) Figures S13(a) and (b) illustrate that the single carboxyl group of each molecule exposed at the surface of the p- and bm-MDBA SAMs has an orientation where one would anticipate that it could interact with a low-index plane of calcite.
Since one carboxyl group of the bm- and m-MDBA molecules is directed into the SAM structure, it is important to note that a herringbone-like arrangement within bm- and m-MDBA monolayers would preclude any hydrogen-bonding interactions between carboxyl groups of neighboring molecules, because they would be directed away from one another. As a consequence, it is unlikely that intra-monolayer hydrogen-bonding interactions between carboxyl groups are responsible for the inflexibility observed for the bm- and m-MDBA SAMs.
4. SCANNING ELECTRON MICROSCOPY DATA & ANALYSIS

Figures S14 and S15 display representative scanning electron micrographs recorded following the crystallization of CaCO₃ on the surface of SAMs prepared from m-MDBA and bm-MDBA respectively on Au(111). Each of the samples presented in figures S14 and S15 were prepared under identical experimental conditions to the CaCO₃ on p-MDBA SAM sample displayed in figure 4 of the full paper. In fact, the crystallization of CaCO₃ on each of the three MDBA monolayers was conducted simultaneously within a single ‘CO₂ in’ crystallization chamber.

The scanning electron micrographs presented in figures S14 and S15 provide a clear demonstration that neither the m-MDBA nor the bm-MDBA monolayers induce preferential nucleation on specific crystallographic faces of calcite. The calcite crystallites exhibit a range of distinct planes of nucleation without any discernible selectivity. Meanwhile, the bm-MDBA monolayers actually support the growth of a higher proportion of vaterite florets than calcite rhombohedra.

Figure S14: Scanning electron micrographs of CaCO₃ crystallites formed on an m-MDBA SAM on Au(111). All four images, (a) through (c), were recorded for different regions of a single sample.

Figure S15: Scanning electron micrographs of CaCO₃ crystallites formed on a bm-MDBA SAMs on Au(111). All four images, (a) through (d), were recorded for different regions of a single sample.
Another contrasting feature of the m- and bm-MDBA SAMs with respect to the p-MDBA monolayers is a significantly reduced nucleation density, which is illustrated by the scanning electron micrographs displayed in figure S16. The nucleation density of calcite rhombohedra observed on the p-MDBA SAMs (figure S16(a)) is much greater than on a bm-MDBA monolayer (figure S16(b), which also reflects the behavior of m-MDBA SAMs) exposed to identical growth conditions. Once again, crystallization on the two monolayers represented by figure S16 was conducted simultaneously within the same experimental ‘CO$_2$ in’ crystallization chamber.

![Figure S16: Scanning electron micrographs of CaCO$_3$ crystallites formed on the surface of (a) a p-MDBA SAM and (b) a bm-MDBA](image)

Figure S17(a) displays a representative scanning electron micrograph recorded for a p-MDBA SAM supporting a surface film of Mg-stabilized ACC (reproduced from the main manuscript). This region of the sample surface encompasses two smaller areas (approximately 150 x 150 nm and 800 x 800 nm respectively) that had been scanned previously. The smaller regions are clearly observed as darker squares towards the center of the micrograph and the color change is attributed to beam damage incurred during prior scanning. Significantly, comparable features were not observed for bare Au(111) (figure S17(b)) nor SAM/Au(111) samples, which indicates that the damage must be incurred by a phase residing on top of the SAM/Au(111), namely the Mg-stabilized ACC mineral. The extent of beam damage provides an indication of the high surface coverage by the mineral phase (> 75%). Such a high surface coverage is significant because it ensures that the carbon K-edge XAS data recorded for the SAM/mineral samples will be dominated by signal from organothiol molecules at the
SAM/mineral interface. Therefore, the XAS spectra will reflect the orientation of the MDBA molecules beneath the Mg-stabilized ACC rather than those that do not support the mineral phase.

Further inspection of the micrograph presented in figure S17(a) reveals that the mineral overlayer is composed of rounded particles approximately 20-50 nm in diameter, which is significantly smaller than the average domain size observed for the bare Au(111) substrate displayed in figure S17(b). The mineral particles bear a qualitative resemblance to the ACC particles of CaCO$_3$ formed on hydroxyl terminated SAMs and are of comparable size. Equally importantly, the size of the Mg-stabilized particles implies that the thickness of the mineral layer is on the order of 20-50nm. Such a thin overlayer is beneficial for XAS studies at the carbon K-edge because it results in limited attenuation of the incident photons by the mineral phase (the attenuation length of 290eV photons through Mg-stabilized CaCO$_3$ is approximately 430 nm at 90° incidence and 150 nm at 20° incidence), thereby enabling direct study of the underlying MDBA SAMs. The less than complete surface coverage of the mineral phase is also valuable because it allows for the escape of secondary electrons into the continuum and, by extension, measurement of x-ray absorption by the SAM using the total electron yield mode.

Figure S17: Scanning electron micrograph recorded for (a) an Mg-stabilized ACC film prepared on the surface of a p-MDBA SAM on Au(111) and (b) a bare, flame-annealed, Au(111) surface. Note that the smallest and darkest square region in (a) has been scanned twice and that the next largest square (which appears to be slightly tilted) has been scanned once before this image was recorded.
5. ATOMIC FORCE MICROSCOPY (AFM)

Methods: Atomic Force Microscopy (AFM) was performed using an AFM fluid cell within multimode AFM (Nanoscope VIII controller, Bruker Nano AXS, Santa Barbara, CA) equipped with liquid resistant, vertical engage 160 µm “J” scanner. The AFM probe consisted of a sharp silicon tip on a rectangular shape silicon nitride cantilever (HYDRA probe, length: 200 µm, width: 35 µm, spring constant $k = \text{ca. } 0.035 \text{ N/m}$, average tip radius $\leq 10 \text{ nm}$, AppNano, Santa Clara, CA). Atomically flat gold substrates were prepared using a template-stripping method. Freshly prepared template stripped Au(111) (TSG) substrates were incubated in ethanol solution of MDBA to form ‘as prepared’ SAM and then immediately glued on metal disks using 20-min epoxy glue. Deionized water (pH 7.2, 18.5 MΩ) was injected into the fluid cell of an AFM and the surfaces of three different SAMs on Au(111) were imaged by contact-mode at 0.5 to 2 Hz scan speed.

Results & Discussion: Figure S17 displays AFM images and height profiles of as prepared p-, m-, and bm-MDBA SAM on Au(111). All three types of MDBA SAM on Au(111) exhibit the formation of domains that have height difference of ca. 2.4 to 3.0 Å. Significantly larger height differences (> 4 Å) between neighboring domains were not observed, although pinholes are evident in all of the experimental samples. The absence of height differences in excess of 4 Å provides strong evidence that there is minimal bilayer formation in the as prepared MDBA SAMs and, as such, the AFM data is consistent with the S(2p) PES data presented in the main paper. Since the length of each MDBA molecule exceeds 18 Å, a height difference of ≤ 4 Å would require the upper molecules in a bilayer structure to lie almost prostrate on the sample surface, tilted by ≥ 77° from the Au(111) surface normal. The formation of this bilayer arrangement is highly unlikely due to the unfavorable steric interactions that would result: at a tilt angle of ≥ 77° for the molecules that compose the upper layer, the non-linear backbone of carbon-to-carbon bonds in the alkyl chains would cause overlap with atoms that compose the surface of the lower layer of molecules (as illustrated in figure S13, above). As such, this bilayer arrangement would be unphysical.
Figure S18: Highly resolved, contact fluid AFM images and height profiles of ‘as prepared’ SAMs on Au(111) of (a) p-MDBA, (b) m-MDBA, (c) bm-MDBA, and (d) bare Au(111) showing similar domain formation. Each AFM image contains its height profile (inset image) measured along a horizontal black dotted line showing the average height difference ($\Delta h$) of ca. 0.24 $\sim$ 0.30 nm measured from between two black triangles in the inset profile.
6. PHOTOEMISSION SPECTROSCOPY (PES)

**Methods:** PES spectra were recorded on beamline 8.2 of the Stanford Synchrotron Radiation Laboratory (SSRL) at the Stanford Linear Accelerator (SLAC) according to well-defined protocols described in the literature. Each spectrum was collected at an incident angle of 20° between the incident beam and the surface of the experimental sample. All PES data was recorded using a PHI15-255G cylindrical mirror analyzer (CMA) and associated OEM electronics. In all cases, the CMA was operated at a pass energy of 25 eV. C(1s) spectra were obtained at an incident photon energy of 400 eV; S(2p)

![Figure S19: Sulfur 2p photoemission spectra for SAMs of each MDBA isomer prepared on Au(111) in an acetic acid (5%) in ethanol (95%) solvent. The red, green and blue spectra correspond to the experimental data recorded for SAMs prepared from each isomer of MDBA (bm-MDBA, m-MDBA and p-MDBA respectively). The best fitting model for each experimental spectrum is displayed as an overlaying dotted black line. The components of each best fitting model are observed below the corresponding experimental data. As an aid in distinguishing between the components of each best fitting model, the 'bound' doublets are presented as a solid black line and the 'elemental', 'unbound' and 'oxidized' doublets are presented as dashed black lines.](image-url)
spectra were obtained at incident photon energies of 280 and 400 eV. For the purposes of energy calibration, a PES spectrum of the Au 4f electrons was recorded immediately after each C(1s) and S(2p) measurement on the same region of the sample surface. The Au(4f\textsubscript{7/2}) photoelectron at 84.01 ± 0.05 eV was then used to convert from kinetic energy to binding energy scales. As for the XAS data, each PES spectrum was recorded from a fresh region of the sample surface to minimize the effects of beam damage to the MDBA SAM samples\textsuperscript{5}. Furthermore, every PES spectrum was recorded in ≤ 3 min.

Results & Discussion: S(2p) PES measurements of all three ‘as prepared’ MDBA SAMs were conducted to obtain insight into their structure, bonding and surface attachment to the Au substrates. Modeling of the experimental data according to protocols described in the literature\textsuperscript{9} enables identification of the relative proportion of sulfur atoms in each of four distinct environments within the SAMs: (1) ‘oxidized’ sulfur, (2) ‘bound’ thiolate, which arises from MDBA molecules that are attached to the Au surface via their sulfur atom, (3) ‘unbound’ mercaptan (i.e. –SH), and (4) ‘elemental’ sulfur. The results of modeling the S2p PES data are displayed in table 1. Au-bound thiolate predominates in each of the MDBA SAMs, accounting for >85% of all sulfur within the monolayers. This is consistent with the proportion of ‘bound’ sulfur observed for carboxyl-terminated alkanethiol SAMs prepared on Au(111) under equivalent conditions\textsuperscript{10}. Significantly, no other environment of sulfur accounts for >10% of the total S2p PES signal.

Figure S19 displays representative S(2p) PES spectra recorded for SAMs prepared from each isomer of MDBA on Au(111), accompanied by best-fitting model spectra. The calculated spectra are composed of four separate S(2p) resonances that correspond to distinct sulfur environments within the SAM and/or close to the surface of the Au substrate. All of the resonances are spin-orbit split into doublets with a branching ratio of ~2:1 and an energy separation of ~1.2 eV. The S\textsubscript{2p\textsubscript{3/2}} (S\textsubscript{2p\textsubscript{1/2}}) resonance observed at the lowest binding energy, 160.8eV (162.0 eV), corresponds to sulfur in an 'elemental' state within the SAM. The neighboring resonance at 161.9eV (163.1eV) is attributed to Au-bound thiolate\textsuperscript{11} and, as a consequence, arises from MDBA molecules that are attached to the Au
surface through their sulfur atom (figure S20) MDBA molecules that do not form an Au-S bond and retain the mercaptan (-SH) functionality correspond to the 'unbound' resonance close to 163.2eV (164.4eV)\textsuperscript{11}. Meanwhile, the final resonance, observed in the region of 167.1eV (168.3eV), arises from 'oxidized' sulfur. Any sample containing > 5% 'oxidized' sulfur was deemed unsuitable for further study due to SAM degradation from exposure to atmospheric oxygen.

![Figure S20: Schematic to illustrate the structure of a p-MDBA-based surface dimer on Au(111) formed via hydrogen bonding between carboxyl groups. The 'bound' molecule is attached to the underlying substrate via an Au-thiolate bond, while the 'unbound' molecule retains the full mercaptan (-SH) group](image)

The integrated relative intensities for each sulfur environment within SAMs prepared from the three isomers of MDBA are provided in table S1. All of the resonance intensities were adjusted to account for photoelectron attenuation by the condensed monolayer using the methodology of Lamont et al.\textsuperscript{12}. Correction for photoelectron attenuation becomes of increasing importance as a function of SAM thickness to ensure an accurate assignment of the relative proportions of sulfur in each environment and is essential for monolayers prepared from long organothiol molecules such as the isomers of MDBA (~20Å). As an illustration, attenuation of photoelectrons emitted from sulfur atoms at the surface of the
Au substrate (e.g. 'bound' sulfur) accounts for a reduction in the total signal intensity of ~ 85% for PES measurements conducted at an incident photon energy of 400eV, whereas photoelectrons from sulfur at/near the upper surface (e.g. 'unbound' sulfur) of the MDBA monolayers experience minimal, if any, attenuation. This phenomenon results in comparable magnitudes for the 'bound' and 'unbound' resonances in the S(2p) spectra, despite the fact that Au-bound thiolate predominates within the MDBA SAMs. In fact, each MDBA SAM contains > 85% 'bound' sulfur and < 6% of either 'unbound' or 'elemental' sulfur.

The S(2p) PES data demonstrates that all three ‘as prepared’ MDBA SAMs are composed primarily of monolayer regions and provides evidence for only limited bilayer formation. The large signal from bound sulfur indicates that the vast majority (> 85%) of MDBA molecules are directly bonded to the Au surface through their terminal sulfur atom, as one would anticipate within a monolayer arrangement. Nonetheless, the presence of both ‘unbound’ and ‘oxidized’ MDBA molecules indicates some deviation from an idealized monolayer structure since these species are not constrained to reside in a single layer adjacent to the substrate surface. The majority of the signal from ‘unbound’ mercaptan and ‘oxidized’ sulfur is attributed to molecules that have dimerized with ‘bound’ molecules at the substrate surface via hydrogen-bonding between the carboxyl groups. The formation of surface dimers is undesirable because it has the effect of burying the carboxyl functionality within a bilayer structure and exposing either a mercaptan group or oxidized sulfur at the surface of the SAM. Even if one assumes that all of the unbound and oxidized dimers form hydrogen bonded surface dimers, a minimum of between 78-84% of each as prepared SAM would still have a monolayer structure, which is a similar fraction to that observed in the carboxyl-terminated alkanethiol monolayers typically used for the investigation of SAM-directed crystallization\textsuperscript{10}. Equally importantly, such close similarity in the S(2p) PES data for the three types of ‘as prepared’ MDBA SAMs indicates that any differences in the degree of bilayer formation or bonding to the Au surface are far too small to be responsible for the contrasting influence the SAMs exert over mineralization.
Characteristic C(1s) PES spectra for all three types of MDBA SAM are presented in figure S21. Each spectrum contains two distinct resonances: the first resonance, observed at 284.2eV, is attributed to the carbon atoms within the alkyl chain and the aromatic ring that are not directly bonded to oxygen. The second resonance arises from the carboxyl carbons and is shifted to higher binding energy (288.5eV) with respect to the first due to the inductive effect of the electronegative carboxyl oxygen atoms. Table 1 displays the integrated intensities for the carboxyl carbon resonance as a percentage of the total carbon content in each MDBA monolayer. The normalized carboxyl carbon content of the bm-MDBA SAMs (14%) determined via analysis of the C(1s) PES spectra is approximately twice as large as in the p-MDBA (8%) and m-MDBA (6%). The 2% increase in normalized carboxyl carbon contribution for the p-MDBA monolayers relative to their m-MDBA analogues is also noteworthy, despite the fact that this difference falls within the experimental error, because it is consistent with an

Figure S21: Carbon 1s photoemission spectra for SAMs of each MDBA isomer prepared on Au(111) in an acetic acid (5%) in ethanol (95%) solvent. The experimental spectra are also overlaid with one another at the top of the graph for the purposes of direct comparison.
endgroup orientation in which the carboxyl group of the m-MDBA is buried within the monolayer. Photoelectrons emitted from the buried carboxyl group of the m-MDBA molecules will undergo greater attenuation by the remainder of the SAM than those emitted from the carboxyl groups of the p-MBDA molecules, which reside at the surface of the monolayer. The result is the reduction in intensity of carboxyl peak in the C(1s) PES spectrum of the m-MDBA SAMs relative to the p-MDBA SAMs.

It is also interesting that the C(1s) PES resonance intensity for the carboxyl groups of the ‘as prepared’ bm-MDBA SAMs is equal to the combined intensities for the ‘as prepared’ p- and m-MDBA SAMs. This result is consistent with the endgroup orientation derived from analysis of the XAS data: photoelectrons from the carboxyl groups of the bm-MDBA molecules exposed and buried within the monolayer will undergo equivalent attenuation to those in the p- and m-MDBA SAMs respectively.

<table>
<thead>
<tr>
<th></th>
<th>S(2p) PES Integrated Intensities</th>
<th>C(1s) PES Integrated Intensities</th>
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<tr>
<td></td>
<td>Elemental sulfur (%)</td>
<td>Bound thiolate (%)</td>
</tr>
<tr>
<td>p-MDBA</td>
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<td>90 ± 3</td>
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<tr>
<td>m-MDBA</td>
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<td>86 ± 6</td>
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<tr>
<td>bm-MDBA</td>
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<td>87 ± 5</td>
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Table S1: Integrated S2p and C1s PES resonance intensities for SAMs of each MDBA isomer prepared on Au(111) in an acetic acid (5%) in ethanol (95%) solvent.
REFERENCES


