

Spatial and Temporal Control over Adsorption from Multicomponent Solutions

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Supplementary Information

(1) Synthesis and characterization

(2) Experimental details

(3) Additional STM images

(1) Synthesis and characterization

All solvents were purchased from Fisher Scientific. All reagents were used as received and were purchased from Acros Organics.

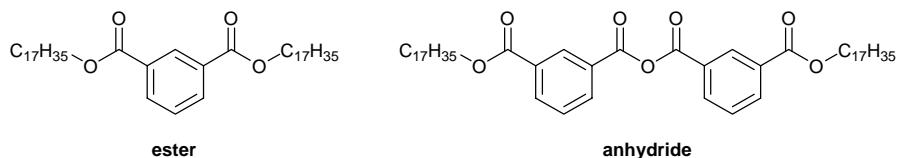
Preparation of diheptadecyl isophthalic anhydride: To degassed, anhydrous CH₂Cl₂ (75 mL) was added triethylamine (0.680 mL, 4.89 mmol), isophthaloyl dichloride (3.073 g, 15.13 mmol), 4-dimethylaminopyridine (0.0437 g, 0.358 mmol), and 1-heptadecanol (1.258 g, 4.90 mmol). The reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. The reaction mixture was diluted with CH₂Cl₂ (50 mL), washed with 1 N HCl (2 × 100 mL) and brine (50 mL), then dried over anhydrous Na₂SO₄. The resultant material was heated to 50 °C under vacuum (< 5 mtorr) in a sublimator with a water condenser to remove unreacted isophthaloyl dichloride, providing 3-chlorocarbonyl benzoic acid heptadecyl ester as a white solid that was used without further purification. To synthesize 1,3-benzenedicarboxylic acid monoheptadecyl ester, 3-chlorocarbonyl benzoic acid heptadecyl ester (2.018 g, 4.77 mmol) was dissolved in 10 mL dimethoxyethane with 1 mL of distilled water and triethylamine (0.68 mL, 4.9 mmol). After 24 hours, the white precipitate was filtered, dissolved in CH₂Cl₂ (50 mL), washed with water (50 mL) and brine (50 mL), then dried over anhydrous Na₂SO₄, providing crude 1,3-benzenedicarboxylic acid monoheptadecyl ester. This material (0.505 g, 1.25 mmol) was combined with crude 3-chlorocarbonyl benzoic acid heptadecyl ester (0.531 g, 1.24 mmol) in dimethoxyethane (50 mL) and triethylamine (0.20 mL, 1.4 mmol). The reaction mixture was stirred overnight and a white precipitate formed. The solvent was removed by rotary evaporation, yielding a white solid (0.896 g, 90%) that was approximately 95% pure. Repeated recrystallization of a portion of this material from acetone and methyl ethyl ketone yielded pure diheptadecyl isophthalic anhydride (12%). mp 82.5–83.2 °C. Found: C 75.8, H 10.0. Calcd for C₅₀H₇₈O₇: C 75.9; H 9.9%; IR (KBr pellet): 2956 (s), 2916 (vs), 2850 (s), 1807 (s), 1724 (s), 1473 (m), 1309 (m), 1286 (m), 1246 (s), 1194 (s), 1122 (m), 1030 (s), 993 (s), 960

(m), 721 (s), 621 (m), 467 (w) cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , δ): 8.80 (t, $J = 1.6$ Hz, 2 H), 8.37 (m, 4 H), 7.64 (t, $J = 7.8$ Hz, 2 H), 4.36 (t, $J = 6.8$ Hz, 4 H), 1.79 (quint, $J = 7.1$ Hz, 4 H), 1.43 (quint, $J = 7.0$ Hz, 4 H), 1.25-1.40 (m, 52 H), 0.87 (t, $J = 6.8$ Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 165.29, 161.41, 135.34, 134.43, 131.63, 131.61, 129.15, 129.12, 65.76, 31.91, 29.68 (broad), 29.66, 29.64, 29.62, 29.57, 29.51, 29.34, 29.26, 28.66, 25.99, 22.67, 14.09. MS (EI): m/z 792.5 (0.35%), 791.5 (1.3), 790.5 (M^+ , 2.4), 387.3 (66.8), 167.0 (100), 149.0 (97.4).

Preparation and characterization of 1,3-diheptadecyl ester has previously been reported (K. E. Plass, K. Kim, and A. J. Matzger, *J. Am. Chem. Soc.*, 2004, **126**, 9042).

(2) Experimental details

A Nanoscope E STM (Digital Instruments) was employed for all imaging. Highly oriented pyrolytic graphite (HOPG) (SPI-1 grade, Structure Probe Inc.) was the substrate for monolayer formation. A 1-2 μL drop of solution in phenyloctane was placed on freshly cleaved HOPG to obtain a self-assembled monolayer. Initial studies used a concentrated solution of diheptadecyl isophthalate and a contaminant identified as diheptadecyl isophthalic anhydride in a 4.2:1 **ester:anhydride** weight ratio (5.2:1: molar ratio). The results were repeated with a 2 μL drop of solution in 1-phenyloctane containing 0.50 mg/mL diheptadecyl isophthalate and 0.050 mg/mL independently synthesized diheptadecyl isophthalic anhydride, resulting in a 10:1 **ester:anhydride** weight ratio (12.3:1 molar ratio). The tips were made from Pt/Ir wire (20% Ir, 0.010 inch diameter, California Fine Wire) by mechanical cutting and shaped *in situ* by applying short 10 V pulses. The quality of the tips was verified by scanning the HOPG surface under the monolayer at reduced bias voltage. All images are unfiltered. STM imaging was performed under ambient conditions and typical STM settings include a set current of 300 pA and an applied bias of 600-1000 mV (sample positive). Desorption experiments were performed by increasing the set current to 3000 pA over approximately one third of the scanned area. Scan rates (the number of lines scanned per second) of 20 Hz and 10 Hz, resulted in 25 s and 50 s delays between each captured image, respectively.



(3) Additional STM images

Figure S1. (A) STM image of an **anhydride** monolayer (100 nm × 100 nm, 10 Hz, 800 mV, 300 pA), which is desorbed by changing the set current to 3000 pA (B). The inset image in (B) and the next image (C) reveal that the monolayer has been disrupted, and remains resolvable only in the upper and lower portions of the scan in areas where the large set current was not applied. (D) In the formerly unresolved area, **ester** monolayer has formed, replacing the **anhydride** monolayer.

