Homologous, Long-chain Alkyl Dendrons Form Homologous Thin Films on Silver Surfaces

André A. Williams, B. Scott Day, Brett L. Kite, Melinda K. McPherson, Carla Slebodnik, John R. Morris,* and Richard D. Gandour*

Supplementary Material

General Comments for Synthetic Work. Melting point data were obtained with a digital melting point apparatus. ¹H and ¹³C NMR spectra were obtained at 500 and 125 MHz, respectively; TMS was used as the internal reference in ¹H spectra. IR spectra were obtained on neat samples with an FTIR equipped with a diamond ATR system. HRMS data were obtained on a dual-sector mass spectrometer in FAB mode with 2-nitrobenzylalcohol as the proton donor. Elemental analyses were performed by Atlantic Microlab, Inc. in Norcross, GA. Solutions were concentrated by rotary evaporation unless specified otherwise. Unless specified, solvents and reagents were used as received. Octadecanoyl chloride and tetradecanoyl choride were synthesized via a reaction of the corresponding carboxylic acid in refluxing thionyl chloride and a few drops of DMF for 24 h. The products were purified by bulb-to-bulb distillation until a clear, colorless liquid was obtained. Di-*tert*-butyl 4-amino-4-[2-(*tert*-

butoxycarbonyl)ethyl]heptanedioate (Behera's Amine) was synthesized as previously described.^{1, 2}

General procedures for long chain tri *tert*-butyl esters, **3EAm#**: **Procedure A**. Behera's amine(12.03 mmol) was dissolved in dry PhH(60 mL). Triethylamine(14.43 mmol) and the



appropriate acid halide(12.63 mmol) were added to the flask. The additions resulted immediately in a cloudy solution. The solution was stirred for 48 h at rt. The reaction mixture was washed with saturated aq NaHCO₃, water, cold 10% aq HCl, and brine. The solution was dried with Na₂SO₄. After filtration, the solution was concentrated yielding an off-white solid, which was recrystallized from EtOH/H₂O to yield white needles or a white solid (77–84%). **Procedure B.** A mixture of the appropriate carboxylic acid(12.03 mmol), Behera's Amine(12.64 mmol), DCC(12.03 mmol), and 1-hydroxybenzotriazole(12.03 mmol) was



dissolved in dry THF(365 mL) and stirred at rt. A white precipitate crashed out of solution after approximately 1 h. The solution was stirred for 7 d. The precipitate was vacuum filtered; the filtrate was concentrated in vacuo. The slightly yellow solid was dissolved in CH_2Cl_2 . The solution was placed in the freezer overnight. The resulting precipitate was again removed by vacuum filtration. The filtrate was washed with cold 10% aq HCl, water, saturated NaHCO₃, and brine. The solution was dried with Na₂SO₄. After filtration, the solvent was concentrated yielding an off-white solid, which was recrystallized from with EtOH/H₂O to yield a white solid (61–82 %).



Di*tert*-**butyl 4-(2-(***tert***-Butoxycarbonyl)ethyl)-4-(1-oxotetradecylamino)heptanedioate, 3EAm13**: The general procedure (A) described above afforded a white solid (5.81 g, 77%); mp 72.8–73.7 °C; ¹H NMR (CDCl₃): δ = 0.87 (t, 3H), 1.24–1.29 (bm, 20H), 1.42 (s, 27H), 1.57 (m, 2H), 1.95 (t, 6H), 2.08 (t, 2H), 2.21 (t, 6H), 5.78 (s, 1H). ¹³C NMR (CDCl₃): δ = 14.19, 22.77, 25.89, 28.14, 29.40, 29.43, 29.45, 29.59, 29.72, 29.90, 30.06, 31.99, 37.71, 57.33, 80.72, 172.72, 173.02. IR: 3358, 2918, 1719, 1709, 1676, 1536, 1147 cm⁻¹. HRMS: for C₃₈H₇₁NO₇ calcd 626.4996, found 626.4981. Anal. Calcd for C₃₆H₆₇NO₇: C, 69.08; H, 10.79; N, 2.24. Found: C, 69.22; H, 10.91; N, 2.34.



Di*-tert*-**butyl 4-(2-(***tert***-Butoxycarbonyl)ethyl)-4-(1-oxohexadecylamino)heptanedioate, 3EAm15**: The general procedure (A) described above afforded a white solid (6.58 g, 84%); mp 62.6–63.3 °C. ¹H NMR (CDCl₃): δ= 0.87 (t, 3H), 1.24–1.29 (bm, 24H), 1.42 (s, 27H), 1.56 (bm, 2H), 1.95 (t, 6H), 2.08 (t, 2H), 2.21 (t, 6H), 5.77 (s, 1H). ¹³C NMR (CDCl₃): δ= 14.17, 22.74, 25.88, 28.12, 29.37, 29.41, 29.43, 29.57, 29.71, 29.75, 29.88, 30.04, 30.18, 31.98, 37.68, 57.32,

80.67, 172.69, 173.00. IR: 3395, 2914, 1730, 1725, 1713, 1669, 1526, 1146 cm⁻¹. HRMS: for C₃₈H₇₁NO₇ calcd 654.5269, found 654.5309. Anal. Calcd for C₃₈H₇₁NO₇: C, 69.79; H, 10.94; N, 2.14; O, 17.12. Found: C, 69.76; H, 10.96; N, 2.21; O, 17.14.



Di*tert*-**butyl 4-(2***tert*-**Butoxycarbonyl)ethyl)-4-(1-oxooctadecylamino)heptanedioate, 3EAm17**: The general procedure (A) described above afforded a white solid (3.99 g, 82%); mp $66.6-67.2 \,^{\circ}C$; ¹H NMR (CDCl₃): δ = 0.87 (t, 3H), 1.22–1.29 (bm, 28H), 1.42 (s, 27H), 1.57, (m, 2H), 1.95 (t, 6H), 2.08 (t, 2H), 2.21 (t, 6H), 5.77 (s, 1H). ¹³C NMR (CDCl₃, 500 MHz): δ = 14.17, 22.74, 25.87, 28.11, 29.37, 29.41, 29.57, 29.71, 29.75, 29.87, 30.03, 31.98, 37.67, 57.31, 80.67, 172.69, 172.99. IR: 3397, 2915, 1730, 1725, 1714, 1670, 1528, 1148 cm⁻¹. HRMS: for C₄₀H₇₅NO₇ calcd 682.5622, found 682.5624. Anal. Calcd for C₄₀H₇₅NO₇: C, 70.44; H, 11.08; N, 2.05. Found: C, 70.56; H, 11.05; N, 2.07.



Di-*tert*-butyl 4-(2-*tert*-Butoxycarbonyl)ethyl)-4-(1-oxoicosylamino)heptanedioate, 3EAm19: The general procedure (B) described above afforded a white solid (7.84 g, 82%); mp 70.6–71.3

°C. ¹H NMR (CDCl₃): δ = 0.87 (t, 3H), 1.22-1.29 (bm, 32H), 1.42 (s, 27H), 1.57 (m, 2H), 1.95 (t, 6H), 2.08 (t, 2H), 2.21 (t, 6H), 5.77 (s, 1H). ¹³C NMR (CDCl₃): δ = 14.18, 22.75, 25.89, 28.14, 29.39, 29.43, 29.44, 29.59, 29.72, 29.76, 29.89, 30.08, 31.99, 37.70, 57.33, 80.70, 172.69, 173.01. IR: 3336, 2914, 1731, 1724, 1713, 1669, 1526, 1147 cm⁻¹. HRMS: for C₄₂H₇₉NO₇ calcd 710.5935, found 710.5923. Anal. Calcd for C₄₂H₇₉NO₇: C, 71.04; H, 11.21; N, 1.97. Found: C, 71.18; H, 11.17; N, 1.98.



Di-tert-butyl 4-(2-tert-Butoxycarbonyl)ethyl)-4-(1-oxodocosylamino)heptanedioate,

3EAm21: The general procedure (B) described above afforded a white solid (5.70 g, 61%); mp 74.7–75.0 °C. ¹H NMR (CDCl₃): δ= 0.87 (t, 3H), 1.24–1.30 (bm, 36H), 1.42 (s, 27H), 1.57 (m, 2H), 1.95 (t, 6H), 2.08 (t, 2H), 2.21 (t, 6H), 5.77 (s, 1H). ¹³C NMR (CDCl₃): δ= 14.20, 22.77, 25.90, 28.15, 29.40, 29.43, 29.60, 29.78, 29.90, 30.08, 32.01, 37.72, 57.34, 80.71, 172.69, 173.01. IR: 3398, 2915, 1731, 1725, 1714, 1670, 1527, 1148. HRMS: for C₃₈H₇₁NO₇ calcd 738.6248, found 738.6212. Anal. Calcd for C₄₄H₈₃NO₇: C, 71.60; H, 11.33; N, 1.90. Found: C, 71.82; H, 11.33; N, 1.97.

General synthesis of long chain triacid: Triesters 3EAm13 and 3EAm15 (12.67 mmol) were



dissolved in a minimal amount of 99% HCOOH and stirred overnight at rt. Cosolvents, THF and acetone were added to formic acid to get triesters **3EAm17–3EAm21** completely into solution; the reactions were stirred overnight at rt. The milky white solution was concentrated in vacuo. The white solid was recrystallized from glacial HOAc/hexane to yield a white solid (65–86%).



4-(2-Carboxyethyl)-4-(1-oxotetradecylamino)heptanedioic Acid, **3**CAm13: Following the general procedure described above, **3**EAm13 (2.00 g, 3.20 mmol) was dissolved in HCOOH (21 mL). Most of the solid dissolved immediately; a small amount of solid remained but slowly went into solution as stirring continued. On work up, the reaction afforded a white solid (1.12 g, 77%); mp 162.7–163.1 °C; ¹H NMR (CD₃OD): δ = 0.89 (t, 3H), 1.20–1.35 (bm, 20H), 1.58 (m, 2H), 2.00 (t, 6H), 2.16 (t, 2H), 2.26 (t, 6H). ¹³C NMR (DMSO): δ = 14.52, 22.65, 26.03, 28.59, 29.15, 29.27, 29.34, 29.53, 29.58, 31.86, 36.39, 56.79, 172.61, 174.99. IR: 3419, 3100, 2916, 1719, 1692, 1651, 1529, 1175 cm⁻¹. HRMS: for C₃₈H₇₁NO₇ calcd 458.3118, found 458.3080. Anal. Calcd for C₂₄H₄₃NO₇: C, 62.99; H, 9.47; N, 3.06. Found: C, 63.02; H, 9.53; N, 3.11.



4-(2-Carboxyethyl)-4-(1-oxohexadecylamino)heptanedioic Acid, 3CAm15: Following the general procedure described above, **3EAm15** (2.33g, 3.56 mmol) was dissolved in HCOOH (100 mL), acetone (70 mL), and THF (50 mL); the solution was filtered to remove a trace amount of

undissolved solids. On work up, the reaction afforded a white solid (1.14 g, 80%); mp 164.5– 165.1 °C. ¹H NMR (CD₃OD) δ = 0.89 (t, 3H), 1.28–1.31 (bm, 24H), 1.58 (bm, 2H), 2.00 (t, 6H), 2.16 (t, 2H), 2.26 (t, 6H). ¹³C NMR (DMSO): δ = 14.51, 22.65, 26.01, 28.59, 29.17, 29.27, 29.35, 29.61, 31.85, 36.40, 56.79, 172.60, 174.98. IR: 3417, 3100, 2915, 1723, 1694, 1636, 1520,1174 cm⁻¹. HRMS: calcd for C₂₆H₄₇NO₇ 486.3431, found 486.3423. Anal. Calcd for C₂₆H₄₇NO₇: C, 64.30; H, 9.75; N, 2.88. Found: C, 64.14; H, 9.74; N, 2.95.



4-(2-Carboxyethyl)-4-(1-oxoicosylamino)heptanedioic Acid, 3CAm17: Following the general procedure described above, **3EAm17** (2.54 g, 2.93 mmol) was dissolved in HCOOH (80 mL) and THF (20 mL). On work up, the reaction afforded a white solid (1.40 g, 73%); mp 162.5–163.8 °C . ¹H NMR (CD₃OD): δ = 0.89 (t, 3H), 1.24–1.31 (bm, 28H), 1.58 (m, 2H), 2.00 (t, 6H), 2.16 (t, 2H), 2.25 (t, 6H). ¹³C NMR (DMSO): δ = 14.52, 22.66, 26.02, 28.59, 29.17, 29.27, 29.36, 29.56, 29.60, 31.85, 36.41, 56.79, 172.60, 174.99. IR: 3418, 3100, 2916, 1720, 1694, 1652, 1521, 1175 cm⁻¹. HRMS: for C₂₈H₅₁NO₇ calcd 514.3744, found 514.3739. Anal. Calcd for C₂₈H₅₁NO₇: C, 64.47; H, 10.01; N, 2.73. Found: C, 64.38; H, 10.16; N, 2.80.



4-(2-Carboxyethyl)-4-(1-oxooctadecylamino)heptanedioic Acid, 3CAm19: Following the general procedure described above, **3EAm19** (2.06 g, 2.90 mmol)was dissolved in HCOOH (125

mL), THF (40 mL), and acetone (30 mL); the solution was filtered to remove a trace amount of undissolved solids. On work up, the reaction afforded a white solid (1.02 g, 65%); mp 165.9–166.9 °C. ¹H NMR (CD₃OD): δ = 0.89 (t, 3H), 1.28-1.31 (bm, 32H), 1.58 (m, 2H), 2.00 (t, 6H), 2.16 (t, 2H), 2.26 (t, 6H). ¹³C NMR (DMSO): δ = 14.51, 22.65, 26.02, 28.59, 29.17, 29.26, 29.36, 29.58, 31.85, 36.41, 56.79, 172.59, 174.98. IR: 3416, 3100, 2916, 1719, 1692, 1651, 1520, 1175. HRMS: for C₃₀H₅₅NO₇ calcd 542.4057, found 542.4052. Anal. Calcd for C₃₀H₅₅NO₇: C, 66.51; H, 10.23; N, 2.59. Found: C, 66.28; H, 10.37; N, 2.66.



4-(2-Carboxyethyl)-4-(1-oxodocosylamino)heptanedioic Acid, 3CAm21: Following the general procedure described above, **3EAm21** (5.69 g, 7.72 mmol) was dissolved in HCOOH (350 mL), THF (40 mL), and acetone (60 mL). On work up, the reaction afforded a white solid (3.77 g, 86%); mp 165.0–165.9 °C. ¹H NMR (CD₃OD): δ= 0.89 (t, 3H), 1.28–1.31 (bm, 36H), 1.58 (m, 2H), 2.00 (t, 6H), 2.16 (t, 2H), 2.26 (t, 6H). ¹³C NMR (DMSO, 500 MHz): δ= 14.50, 22.65, 26.02, 28.59, 29.18, 29.27, 29.37, 29.56, 31.24, 31.85, 36.41, 56.78, 172.59, 174.98. IR: 3419, 3100, 2916, 1719, 1692, 1651, 1520, 1175. HRMS: for C₃₂H₅₉NO₇ calcd 570.4370, found 570.4354. Anal. Calcd for C₃₂H₅₉NO₇: C, 67.45; H, 10.44; N, 2.46. Found: C, 67.22; H, 10.60; N, 2.52.

X-ray Analysis of 3EAm15.

Long thin needles (~1.0 x 0.2 x 0.01 mm³) were grown from slow cooling an ethanol/water solution. A needle was cut (~0.23 x 0.18 x 0.011 mm³), mounted on a nylon CryoLoopTM (Hampton Research) with Krytox® Oil (DuPont) and centered on the goniometer of a Oxford

Diffraction XCalibur2[™] diffractometer equipped with a Sapphire[™] CCD detector. The data collection routine, unit cell refinement, and data processing were all carried out with the program CrysAlis.³ Unit cell dimensions were consistent with the triclinic system and the space group PT was assigned. The structure was solved by direct methods and refined using the SHELXTL NT program package.⁴ The final refinement involved an anisotropic model for all non-hydrogen atoms. Idealized hydrogen atom positions and thermal parameters were calculated. The SHELXTL NT program was used for molecular graphics generation.

Table. Crystal data and structure refinement for 3EAm15.			
Empirical formula	C ₃₈ H ₇₁ NO ₇		
Formula weight	653.96		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	PĪ		
Unit cell dimensions	a = 5.6653(9) Å	$\alpha = 82.928(8)^{\circ}$	
	b = 9.9138(10) Å	$\beta = 89.815(10)^{\circ}$	
	c = 35.868(3) Å	$\gamma = 81.801(10)^{\circ}$	
Volume	1978.6(4) Å ³		
Ζ	2		
Density (calculated)	1.098 Mg/m ³		
Absorption coefficient	0.074 mm ⁻¹		
F(000)	724		
Crystal size	0.23 x 0.18 x 0.011 mm ³		
Theta range for data collection	2.86 to 25.05°.		
Index ranges	$-6 \le h \le 4, -11 \le k \le 11, -42 \le l \le 42$		
Reflections collected	13578		
Independent reflections	7015 [R(int) = 0.0706]		
Completeness to theta = 25.05°	99.8 %		
Absorption correction	None		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	7015 / 0 / 425		
Goodness-of-fit on F ²	1.022		
Final R indices $[I \ge 2\sigma(I)]$	R1 = 0.0658, wR2 = 0.1215		
R indices (all data)	R1 = 0.1205, wR2 = 0.1396		
Largest diff. peak and hole 0.243 and -0.250 e.Å ⁻³			

X-ray analysis of 3CAm13.

Colorless plates (0.33 x 0.27 x 0.01 mm3) were crystallized from acetic acid/hexane at rt. The chosen crystal was mounted on a nylon CryoLoop[™] (Hampton Research) with Krytox® Oil (DuPont) and centered on the goniometer of an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 2 CCD detector. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis.⁵ The Laue symmetry was consistent with the triclinic space group PT. Upon indexing the strongest reflections, it was clear that nonmerohedral twinning was present. Refinement of the UB matrices for the two twin domains showed the twin law to be a 180° rotation about the a-axis. The twinning option of CrysAlis was used to process the data for both orientations. The structure was solved by direct methods (SHELXTL NT⁴) using the data from the major twin component. The final structure refinement was performed using an HKLF 5 format file for twin refinement (SHELXTL NT⁴). The asymmetric unit of the structure comprises 2 crystallographically independent molecules. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. The SHELXTL NT was used for molecular graphics generation.

Table. Crystal data and structure refinement for 3CAm13.			
Identification code	cs661		
Empirical formula	$C_{24}H_{43}NO_7$		
Formula weight	457.59		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	PĪ		
Unit cell dimensions	a = 5.4497(8) Å	$\alpha = 93.557(11)^{\circ}$.	
	b = 15.755(2) Å	$\beta = 91.632(11)^{\circ}.$	
	c = 29.520(4) Å	$\gamma = 91.894(12)^{\circ}$.	
Volume	2527.2(6) Å ³		
Ζ	4		
Density (calculated)	1.203 Mg/m ³		
Absorption coefficient	0.087 mm ⁻¹		
F(000)	1000		
Crystal size	0.33 x 0.27 x 0.01 mm ³		
Theta range for data collection	3.91 to 25.00°.		
Index ranges	-6<=h<=6, -18<=k<=18, -35<=l<=35		
Reflections collected	18103		
Independent reflections	8931 [R(int) not calculated due to twin refinement]		
Completeness to theta = 25.00°	99.1 %		
Absorption correction	None		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	18103 / 0 / 588		
Goodness-of-fit on F ²	1.631		
Final R indices $[I \ge 2\sigma(I)]$	R1 = 0.1253, $wR2 = 0.3922$		
R indices (all data)	R1 = 0.1439, wR2 = 0.4168		
Largest diff. peak and hole	0.697 and -0.623 e.Å ⁻³		

Preparation of Thin Films.

A freshly prepared silver oxide sample (evaporated silver on annealed mica, according to Grunwaldt et al.⁶ was immersed in a 1-*mM* solution of a particular triacid (**3CAm#**) in ethanol for 18 hrs. Upon removal of the silver sample from solution, the surface was rinsed extensively in absolute ethanol and dried completely in a high-pressure stream of ultra-pure nitrogen.

RAIR Spectral Analysis of Thin Films.

RAIRS was performed with a Bruker IFS 66v/S spectrometer. Spectra were collected using p-

polarized light at an incident angle of 86° and a liquid-N2-cooled MCT (mercury-cadmium-

telluride) detector. Clean gold substrates were used as background references. Each spectrum

was collected using a minimum resolution of 2 cm^{-1} and is the average of 100 scans.

- 1 G. R. Newkome, R. K. Behera, C. N. Moorefield, and G. R. Baker, *J. Org. Chem.*, 1991, 56, 7162.
- 2 G. R. Newkome and C. D. Weis, Org. Prep. Proced. Int., 1996, 28, 495.
- 3 CrysAlis v1.170, Wroclaw, Poland, 2002
- 4 G. M. Sheldrick, SHELXTL NT ver. 6.12, Madison, WI, 2001
- 5 CrysAlis v1.171, Wroclaw, Poland, 2004
- J. D. Grunwaldt, F. Atamny, U. Gobel, and A. Baiker, *Appl Surf Sci*, 1996, 99, 353.