Homologous, long-chain alkyl dendrons form homologous thin films on silver oxide surfaces†

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As suggested by X-ray crystal structures, homologous, long-chain alkyl dendrons with three carboxyl groups form thin films on silver oxide surfaces, which give reflection–absorption infrared spectra that show a linear increase in intensities of methylene C–H stretching absorptions.

Thin films and self-assembled monolayers (SAMs) have potential applications in materials science and biological sensors.[1] Interest in thin films resides in their potential as inexpensive, versatile surface coatings for applications including the control of wetting and adhesion, chemical and microbial resistance, biocompatibility, and molecular recognition for sensors, especially those related to biology.[2] From our own perspective,[3,4] SAMs serve as well-ordered models for investigating gas–surface collisional dynamics. Most SAMs involve the attachment of thiol compounds to a gold surface to form an ordered structure. Other approaches include attaching terminal alkenes to silica and attaching chlorosilanes, phosphonic acids, phosphonate esters, carboxylate esters, carboxylic acids and alcohols to non-metals and metals that have a native oxide layer.

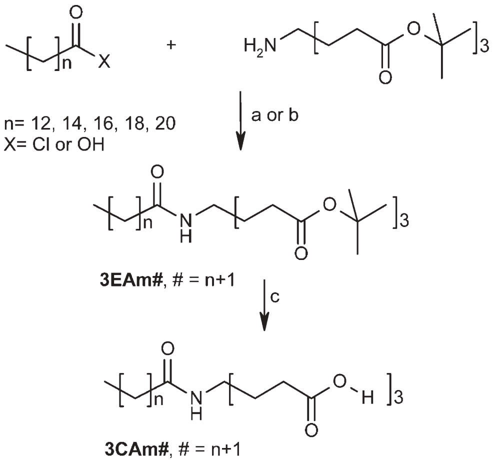
Dendrons and dendrimers have been used to attach molecules to surfaces. The strategy employs the dendron as a tripod or multi-pod,[5] which is attached to a large, bulky molecule. Rigid tripodal ligands have been used to attach dyes to semiconductor nanoparticles.[6] Newkome-type dendrons (first, second and third generation) that terminate with carboxylates have been used to attach a ferrocene in close proximity to a gold electrode that is coated with ammonio-terminated thiols.[7]

Newkome-type dendrons are also used to impart water solubility on very hydrophobic aromatic groups.[8] Amphiphiles that contain second generation Newkome-type dendrons, and lipophilic tails attached to fullerene[9,10] and calixarene,[11] have also been made; the latter forming a persistent micelle.[11] While the water-solubilizing properties of Newkome-type dendrons initiated this project, the discovery of the facile formation of a thin film on a silver oxide surface forms the basis of this report, which begins with their synthesis and single crystal X-ray analyses.

Interest in systematically exploring the aqueous properties of amphiphiles with very long alkyl chains led us to synthesize an even-numbered homologous series, **3CAm#**, of amphiphiles (Scheme 1). With long reaction times, the condensation of Behera's amine[12] with either an acid chloride or a carboxylic acid, which was activated by DCC, afforded the triesters, **3EAm#**, in good to moderate yields of purified products. In general, the acid chloride reaction gave higher yields than the DCC method. Formolysis of the triesters produced the triacids, **3CAm#**, in high yields of recrystallized products. All compounds were fully characterized.†

In the process of synthesizing these amphiphiles, **3EAm15** formed crystals suitable for X-ray analysis.†§ Examination of the packing diagram (Fig. 1a) suggested that parallel alkyl chains packed closely enough to resemble a SAM. In addition, we obtained a lower quality crystal structure of **3CAm13**, which revealed strong hydrogen bonding between neighbouring molecules.

Fig. 1a illustrates for **3EAm15** the crystalline nature of the closely packed alkyl chains. This close packing is critical for self-assembly. Anti-parallel chains pack closer than parallel chains (see Fig. 1 legend). The head group is quite large (cross-sectional area, $a = 243$ Å^2) compared to the length ($l_c = 20.5$ Å) and volume of the chain ($v = 430.9$ Å^3); the packing parameter P[13] ($P = v/al_c$) is 0.089, which predicts a highly curved packing arrangement. This structure illustrates how large head groups pack to accommodate alkyl chain packing. As illustrated in Fig. 1a, the head groups on adjacent molecules in one parallel sheet nestle together. Within a



Scheme 1 Reagents and conditions (% isolated yield). a: X = Cl, TEA, dry PhH, 48 h, rt (77–84%); b: X = OH, DCC, HOBt, dry THF, 7 d, rt (61–82%); c: 99% HCOOH, 18 h, rt (65–86%). Nomenclature: 3E (three –$CH_2CH_2COO^tBu$), 3C (three –CH_2CH_2COOH), Am (amido, –CONH–).

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‡ Please contact John Morris about the surface studies or Richard Gandour about the synthetic aspects of this work.

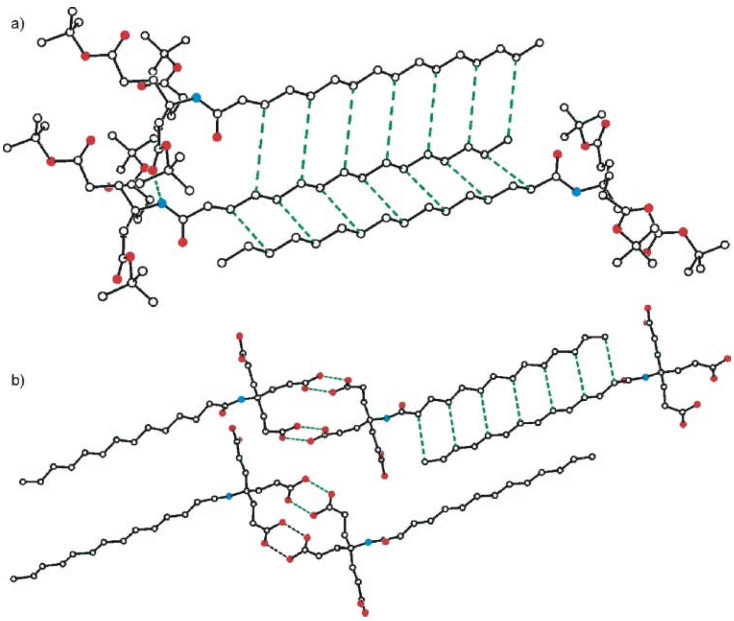

Fig. 1 (a) X-Ray crystal structure of **3EAm15**. This view illustrates that anti-parallel chains pack more closely than parallel chains. For anti-parallel chains, every other carbon lies close to a corresponding carbon in the neighbouring chain; C···C distances range from 4.00–4.12 Å. For parallel chains, all the carbons lie approximately the same distance apart; C···C distances range from 4.96–5.14 Å. An intermolecular hydrogen bond between the amide N–H (blue sphere) on one molecule and an ester carbonyl oxygen (red sphere) on a parallel neighbouring molecule is indicated by a dashed line. The N···O distance is 2.970(3) Å and the N–H···O angle is estimated to be 120.3°. (b) X-Ray crystal structure of **3CAm13**. The chain packing illustrates that anti-parallel chains pack significantly closer than parallel chains. For anti-parallel chains, every other carbon lies close to a corresponding carbon in the neighbouring chain, dashed green lines indicate the C···C distance (3.88–4.12 Å). Six strong intermolecular hydrogen bonds form with four neighbouring molecules. There are four acid–acid (O···O distances, 2.636(4)–2.656(4) Å) and two acid–amide (O···O distances, 2.676(4) and 2.660(4) Å) hydrogen bonds (not shown). In the latter, the acid O–H is the donor and the amide carbonyl oxygen is the acceptor.

parallel sheet, a hydrogen bond connects two head groups, with the amide hydrogen as the donor and an ester-carbonyl oxygen as the acceptor.

Fig. 1b illustrates the alkyl chain packing and hydrogen bonding for **3CAm13**. Anti-parallel chains pack significantly closer than parallel chains. All three carboxyls of the head group are involved in hydrogen bonding. Two carboxyls on each head form acid dimers with a molecule in an adjacent unit cell. The third carboxyl forms a hydrogen bond with a neighbouring molecule; the carboxyl hydrogen as the donor and the amide oxygen as the acceptor.

The close packing of alkyl chains in the above crystal structures suggests a possible arrangement for thin film formation on a surface. Given the tripodal arrangement of carboxyls in **3CAm#**, all three carboxyls could not attach to the surface; the footprint being too large for close packing of parallel alkyl chains. As suggested by Fig. 1b, a carboxyl group could assist in the self-assembly through lateral hydrogen bonding with a neighbouring molecule.

Long-chain fatty acids often form well-ordered, densely-packed SAMs on the native oxide surface of silver.[14–17] The packing structures of **3EAm15** and **3CAm13** in the bulk crystal suggests that monolayers or bilayers may also form on silver oxide. We have explored this possibility by immersing a freshly prepared silver oxide sample (evaporated silver on annealed mica[18]) in a 1 mM ethanolic solution of a particular triacid for 18 h. 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.

Fig. 2a shows reflection absorption infrared spectra (RAIRS), recorded for a series of adsorbed acids (**3CAm#**, where # = 13, 15, 17, 19 and 21). The spectra show narrow, intense peaks for the CH_2 symmetric and asymmetric stretches located at 2856 cm^{-1} and 2928 cm^{-1}, which resemble those for alkanes in liquids.[19] The intensities of the methylene peaks are consistent with those expected for a uniform layer, or layers, of alkane chains on the surface.[19,20] However, these thin films lack the highly ordered structure often observed for long chain fatty acids on silver. Ordered SAMs are evident from a red-shifted methylene asymmetric stretch[19] below about 2920 cm^{-1} and clearly resolved methyl stretches at 2965 cm^{-1} and 2885 cm^{-1}. The lack of order in these systems is attributed to the large footprint of the bulky head groups and competition between surface adsorption and chain–chain hydrogen bonding interactions of neighbouring carboxylic acids. Despite the disordered nature of the system however, the molecules do resist extensive rinsing with ethanol and appear to form a stable thin film. Fig. 2b demonstrates that the methylene stretching intensity is directly proportional to the number of methylenes in the triacid used to make the film. The linear dependence of the methylene peak intensity on chain length demonstrates that the overall coverage and density of acids adsorbed on each surface is constant, a characteristic of uniform molecular adsorption on a surface. This uniform absorption could be either a monolayer, bilayer or multilayer thin film. Future studies will more fully characterize these thin films and find ways to drive an ordered assembly of tripodal molecules.

Given the relative ease of synthesis of these dendrons, one can readily imagine several strategies for expanding this project. One

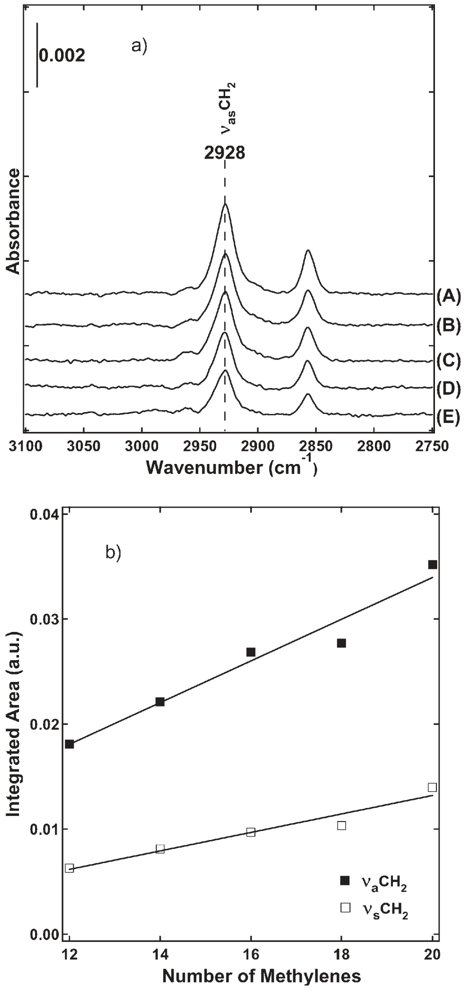

Fig. 2 RAIRS analysis of an Ag surface covered with **3CAm#**. (a) Spectra of # = 21 (A), 19 (B), 17 (C), 15 (D) and 13 (E) from 2750–3100 cm^{-1}. Vertical bar in top-left corner indicates the scale in absorbance units. (b) Integrated intensities of two methylene signals *vs.* the number of methylenes. The number of methylenes in a chain = # − 1.

key step will be in creating a stable thin film. The ease of synthesis of Newkome-type dendrons with ω-functionalized alkyl chains[21] offers great promise and avoids some of the synthetic challenges of thiol chemistry, *viz.*, the ease of oxidation of the thiol group. The discovery of thin film formation in these first generation, tripodal dendrons suggests that thin film formation with other dendrons on other solid surfaces deserves examination.

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Notes and references

§ Crystal data for **3EAm15**: Empirical formula = $C_{38}H_{71}NO_7$, formula weight = 653.96, crystal system = triclinic, space group = $P\bar{1}$, a = 5.6653(9), b = 9.9138(10), c = 35.868(3) Å, α = 82.928(8), β = 89.815(10), γ = 81.801(10)ō, unit cell volume = 1978.6(4) Å^3, Z = 2, absorption coefficient = 0.074 mm^{-1}, reflections collected = 13578, independent reflections = 7015 (R_{int} = 0.0706), final R indices [I>2*ü* (I)] $R1$ = 0.0658 $wR2$ = 0.1215, CCDC 271916. Crystal data for **3CAm13**: Empirical formula = $C_{24}H_{43}NO_7$, formula weight = 457.59, crystal system = triclinic, space group = $P\bar{1}$, a = 5.4497(8), b = 15.755(2), c = 29.520(4) Å, α = 93.557(11), β = 91.632(11), γ = 91.894(12)ō, unit cell volume = 2527.2(6) Å^3, Z = 4, absorption coefficient = 0.087 mm^{-1}, reflections collected = 18103, independent reflections = 8931 (R_{int} not calculated due to twin refinement), final R indices [I>2*ü* (I)] $R1$ = 0.1253 $wR2$ = 0.3922, CCDC 271917. See http://dx.doi.org/10.1039/b506710c for crystallographic data in CIF or other electronic format.

1 A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.
2 M. Mrksich, *Chem. Soc. Rev.*, 2000, **29**, 267.
3 B. S. Day, S. F. Shuler, A. Ducre and J. R. Morris, *J. Chem. Phys.*, 2003, **119**, 8084.
4 M. K. Ferguson, J. R. Lohr, B. S. Day and J. R. Morris, *Phys. Rev. Lett.*, 2004, 92.
5 J. K. Whitesell and H. K. Chang, *Science*, 1993, **261**, 73.
6 E. Galoppini, *Coord. Chem. Rev.*, 2004, **248**, 1283.
7 Y. Wang, C. M. Cardona and A. E. Kaifer, *J. Am. Chem. Soc.*, 1999, **121**, 9756.
8 W. Ong, M. Gomez-Kaifer and A. E. Kaifer, *Chem. Commun.*, 2004, 1677.
9 M. Brettreich, S. Burghardt, C. Bottcher, T. Bayerl, S. Bayerl and A. Hirsch, *Angew. Chem., Int. Ed.*, 2000, **39**, 1845.
10 M. Braun, S. Atalick, D. M. Guldi, H. Lanig, M. Brettreich, S. Burghardt, M. Hatzimarinaki, E. Ravanelli, M. Prato, R. van Eldik and A. Hirsch, *Chem.–Eur. J.*, 2003, **9**, 3867.
11 M. Kellermann, W. Bauer, A. Hirsch, B. Schade, K. Ludwig and C. Bottcher, *Angew. Chem., Int. Ed.*, 2004, **43**, 2959.
12 G. R. Newkome, R. K. Behera, C. N. Moorefield and G. R. Baker, *J. Org. Chem.*, 1991, **56**, 7162.
13 J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1525.
14 D. L. Allara and R. G. Nuzzo, *Langmuir*, 1985, **1**, 45.
15 D. L. Allara and R. G. Nuzzo, *Langmuir*, 1985, **1**, 52.
16 L. K. Chau and M. D. Porter, *Chem. Phys. Lett.*, 1990, **167**, 198.
17 Y. T. Tao, *J. Am. Chem. Soc.*, 1993, **115**, 4350.
18 J. D. Grunwaldt, F. Atamny, U. Gobel and A. Baiker, *Appl. Surf. Sci.*, 1996, **99**, 353.
19 M. D. Porter, T. B. Bright, D. L. Allara and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1987, **109**, 3559.
20 P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. T. Tao, A. N. Parikh and R. G. Nuzzo, *J. Am. Chem. Soc.*, 1991, **113**, 7152.
21 G. R. Newkome, E. F. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689.