Oligofunctional amphiphiles featuring geometric core group preorganization: synthesis and study of Langmuir and Langmuir–Blodgett films†

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Based on the principle of supramolecular preorganization, a new type of oligofunctional amphiphile, of which compounds **1–4** are representative structures, has been designed and synthesized. The typical feature of their structure is a highly rigid and geometrically well-defined central unit composed of ethynylene substituted aromatic spacers with different numbers of amphiphilic segment groups (also of a rigid geometric design) attached to it. The molecules form well-defined Langmuir films when spread from a solution at the air/water interface or when a 10^{-4} M aqueous $CaCl_2$ solution was used as the subphase. By analysis of the surface pressure–surface area (π–A) isotherms, information on the packing behavior and orientation of the amphiphilic molecules depending on the molecular structure could be obtained. Morphological characterization of the dynamic process of monolayer compression at the air/water interface was carried out by Brewster angle microscopy, illustrating several phase states visualized as snap shots. Thin monolayer films produced on a 10^{-4} M aqueous $CaCl_2$ subphase can be transferred to a mica solid support by the Langmuir–Blodgett technique. Tapping mode atomic force microscopy reveals a surface topography of the monofilms composed of **1** and **3** that differ in roughness and also in the properties of elasticity, hardness and adhesive strength. X-Ray crystal structure analysis of three relevant intermediate compounds of the synthesis were successfully determined giving an indication of the potential structural features inherent in the new amphiphiles.

Introduction

The design and construction of molecular materials assembled in organized structures with desirable functions and properties is an area of great interest both from theoretical and applicational aspects.[1,2] Within this frame, thin-film materials have recently attracted considerable attention due to the exciting possibilities for use in optoelectronic, data storage and sensor devices.[3] Materials of this type require the rational design of molecular components that are programmed to assemble through noncovalent intermolecular forces classified as supramolecular interactions.[4] Amphiphiles or surfactants are among the most versatile examples of two-dimensional ordered systems.[5] When spread from a solution at the air/water interface, molecules of this type may form well-defined Langmuir films[6] which can be transferred to solid supports by the Langmuir–Blodgett (LB) technique.[7] This allows an elegant means of building up ultra-thin films of amphiphilic molecules of lamellar order engineered at the molecular level, thereby offering promising access to novel supramolecular architectures and device structures.[8]

Rational engineering of new amphiphiles may arise from a strict geometric instruction aiming at a particular molecular shape and with specific functionality in mind.[9] This way of handling is an equivalent to the principle of preorganization widely used in supramolecular receptors and complexants[4,10] which is also followed here, thus producing a new type of largely shape-persistent and geometrically controlled oligofunctional amphiphiles as sketched in Scheme 1 and of which compounds **1–4** (Schemes 1 and 2) show representative structures.
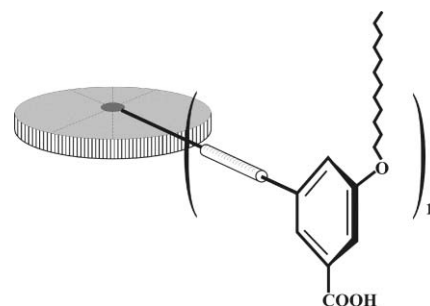

Scheme 1 Structural design concept.

We describe the synthesis of these compounds, report on their ability to form Langmuir and Langmuir–Blodgett films on different subphases, including packing behavior, film stability and morphological properties. We also deal with a discussion of crystal structures that have been obtained from three relevant intermediates belonging to the synthetic pathway of the target compounds.

Results and discussion

Developmental strategy of compound structures

However great in number the known amphiphilic compounds are (including previous oligofunctional species[9,11]) that have been used in the formation of Langmuir films[5,8], in most cases they feature a rather flexible structure arising from particular building elements.[12] On the other hand, highly rigid molecules and shape-persistent architectures have recently proven very productive in supramolecular chemistry and nanomaterials research.[1–4] Thus, structural preorganization has become an
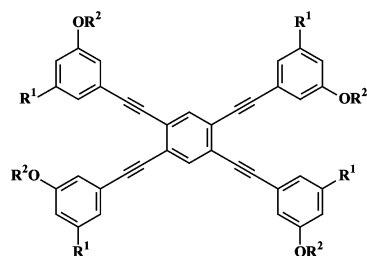
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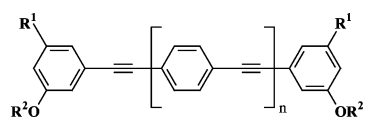
	n	R[1]	R[2]
1	1	COOH	$C_{12}H_{25}$
2	2	COOH	$C_{12}H_{25}$
5a	1	$COOC_2H_5$	H
5b	1	$COOC_2H_5$	$C_{12}H_{25}$
6a	2	$COOC_2H_5$	H
6b	2	$COOC_2H_5$	$C_{12}H_{25}$
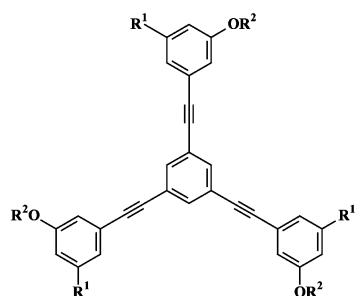
	R[1]	R[2]
3	COOH	$C_{12}H_{25}$
7a	$COOC_2H_5$	H
7b	$COOC_2H_5$	$C_{12}H_{25}$

	R[1]	R[2]
4	COOH	$C_{12}H_{25}$
8a	$COOC_2H_5$	H
8b	$COOC_2H_5$	$C_{12}H_{25}$

Scheme 2 Structures of amphiphilic compounds in this study.

essential cornerstone in this field of development, here meaning the use of structurally defined building blocks to create a molecular backbone that is prevented from collapse, but is highly organized for a particular target.[13] This principle is applied to the present structural design which is based on the attachment of different numbers of amphiphilic segment groups to a rigid and geometrically well-defined central unit, giving rise to a new type of preorganized oligofunctional amphiphiles (Scheme 1). Here, the high degree of shape-persistency is obtained by the use of particularly rigid and strictly geometrical defined aromatic and ethynylene spacer units, including also aromatic carboxylic acid groups that contain the lateral alkyl chains in a fixed position as specified with compounds **1–4** (Schemes 2 and 3).
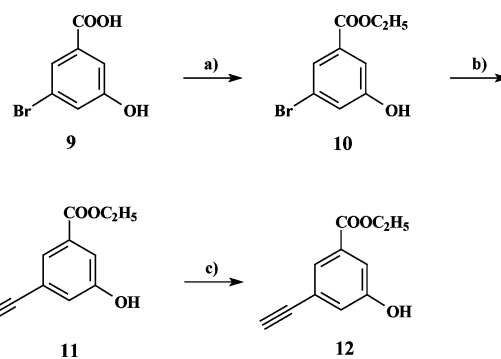
Scheme 3 Synthesis of the lateral building block; (a) EtOH, H_2SO_4; (b) TMS–acetylene, $Pd(OAc)_2$, Ph_3P, CuI, Et_3N; (c) $KF \cdot H_2O$, DMF.
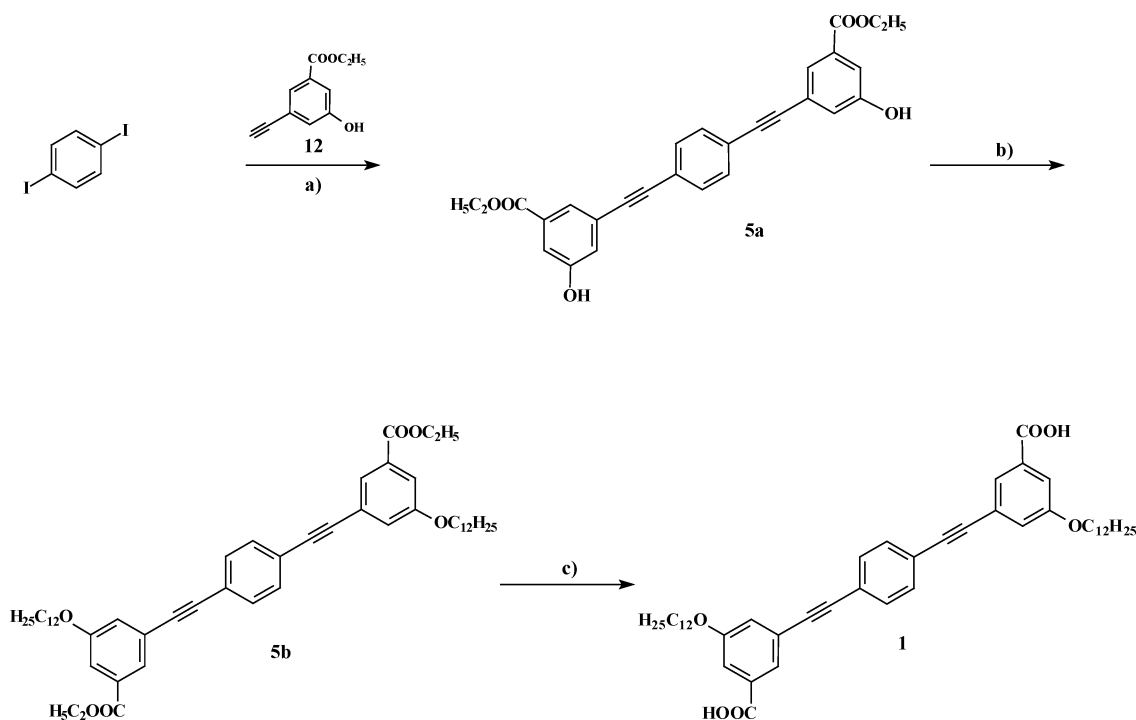
Synthesis

The synthesis of the amphiphilic preorganized compounds **1–4** was performed by Pd-assisted coupling[14] as a key reaction step. In principle, the coupling may be achieved in two opposite ways differing in the distribution of the ethynyl and bromo functions among the educt species, *i.e.* the lateral or the aromatic unit. However, since the palladium cross-coupling between the ethynylated aromatic core and the halogen substituted lateral building block failed, the alternative route of ethynyl and halogen substituent distribution was employed.

The reaction path for the preparation of the amphiphilic target compounds is a multi step procedure, examples are outlined in Schemes 3 and 4 for compound **1**. In order to realize the particular topological structures of **1–4**, shape-persistent central units with linear, extended linear, trigonal and tetragonal geometry were applied, allowing defined positioning of the amphiphilic side groups. Along these lines, commercially available 1,4-diiodobenzene was used as short linear construction element while the extended linear building block is given by bis(4-bromophenyl)acetylene. This latter compound was synthesized (48%) in two steps by direct bromination of diphenylethane in water–acetic acid followed by twofold dehydrohalogenation of the dibromo adduct with sodium ethoxide in ethanol according to the literature procedures.[15,16] In the case of the trigonal core unit, 1,3,5-triiodobenzene was used as the preferred reaction component because of the higher reactivity compared to the bromo derivative. Transformation of the 1,3,5-tribromobenzene into the analogous iodo compound (72%) was achieved by halogen exchange reaction using nickel powder, potassium iodide and iodine in anhydrous DMF.[17] For the same reason, 1,2,4,5-tetraiodobenzene providing the tetragonal building unit was prepared from benzene (67%) by application of the direct iodination procedure using periodic acid and potassium iodide in concentrated sulfuric acid.[18]

The preparation of the lateral building block, properly functionalized for attachment to the central unit and acting as mediator element between hydrophilic and hydrophobic functionalities, is also a multistep reaction (Scheme 3). The starting material, 3-nitrobenzoic acid, was first converted into 3-bromo-5-nitrobenzoic acid (83%) by direct bromination under strongly acidic conditions using silver sulfate in concentrated sulfuric acid.[19] Subsequent reduction of the nitro group with Sn powder and hydrochloric acid gave the corresponding amino compound in 88% yield, which was transferred *via* the diazonium salt to 3-bromo-5-hydroxybenzoic acid (**9**) in 86% yield.[19]

Protective esterification of **9** was carried out with ethanol and concentrated sulfuric acid[20] to obtain **10** in 90% yield. For affixing of the terminal ethynyl unit to **10**, monoprotected trimethylsilylacetylene was used and reacted under palladium catalyzed coupling conditions[21] followed by cleavage of the protecting group.[22] The coupling reaction was carried out under argon in boiling triethylamine with a mixture of catalyst, composed of triphenylphosphane, Pd(II) acetate and

Scheme 4 Example synthesis of compound **1**; (a) **12**, Pd(CH₃COO)₂, PPh₃, CuI, diethyl amine, Ar; (b) $C_{12}H_{25}Br$, K_2CO_3, 18-crown-6, butanone; (c) NaOH, EtOH–H_2O.

Cu(I) iodide to yield 85% of compound **11**. Cleavage of the trimethylsilyl protecting group was performed using KF·H_2O in dimethylformamide to give the lateral building block **12** in almost quantitative yield.

This latter building unit (**12**) was then coupled with the respective di-, tri- and tetrahalogenated central construction elements according to the palladium catalyzed standard procedures,[14,21] yielding 64–74% of the corresponding esters **5a**–**8a**. The lipophilic alkyl chains were introduced to **5a**–**8a** by ether linkage which was carried out with 1-bromododecane and anhydrous potassium carbonate in 2-butanone catalyzed by 18-crown-6[23] to yield **5b**–**8b**, respectively. In the final reaction step, the esters **5b**–**8b** were hydrolyzed with aqueous 1 N sodium hydroxide in boiling ethanol–water[24] to give the amphiphilic target compounds **1**–**4** in 80–82% yield. They are rather high melting solids that show the expected spectroscopic data. All synthesized compounds were characterized by ¹H and ¹³C NMR, IR, MS and elemental analysis.

Langmuir films of the oligofunctional amphiphiles

The new compounds have been designed in the light of their potential use for monolayer formation on the water surface. Examination of the adsorptive behavior at the air/water interface is regarded as one of the effective methods for understanding the relation between the surface active properties and the molecular structure.[5,25] Moreover, analysis of the surface pressure (π–A) isotherms of the Langmuir films makes available much information on the orientation of the amphiphilic molecules at the interface as well as their packing behavior in the film.[9,26]

The compression isotherms of the new preorganized amphiphiles **1**–**4** which were measured on a water and a 10^{-4} M aqueous $CaCl_2$ subphase, recorded on a Langmuir film balance, are shown in Fig. 1 and 2, respectively. Although the collective feature derived from the traces of the respective isotherms is the formation of monomolecular films of relatively high stability, the shapes of the isotherms are distinctly different. This suggests that the monolayers and monolayer polymorphism are different for compounds **1**–**4**, dependent on the molecular structure and the used subphase.[27]
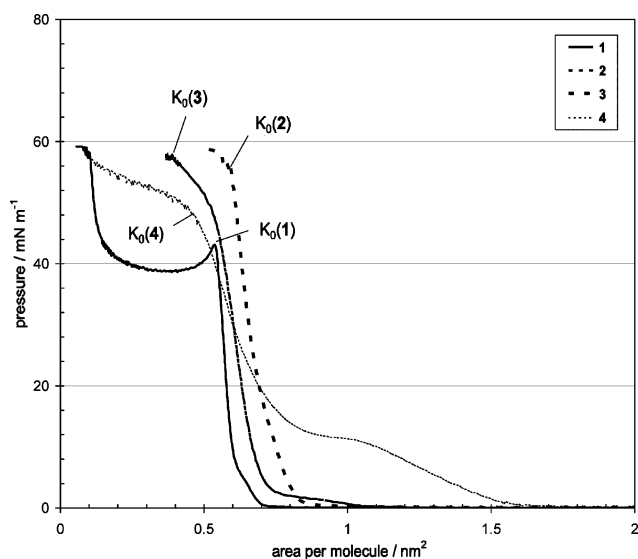
Fig. 1 Isotherms (π–A) of the oligofunctional compounds **1**–**4** on a pure water subphase at 25 °C.

In the case of compound **1**, the first interaction between the molecules of the linear bifunctional amphiphile, lying flat on the surface of the water subphase, was detected at an area per molecule of 0.75 nm², referred to as the lift-off area (Table 1). Further compression of the monolayer leads to the liquid condensed state at an area per molecule of 0.7–0.6 nm² to pass into the solid–condensed state at an area of 0.6 nm² (8 mN m⁻¹), which is characterized by a steep rise of the monolayer pressure. Near the collapse point (K_0) the molecules are arranged in a most dense packing and the monolayer exhibits solid-state analogues properties. Extrapolating the linear part of the isotherm to the film pressure (π = 0 mN m⁻¹), the average required space per molecule (A_0) can be estimated. At the collapse point K_0, the existence of the monolayer ends and further compression leads to formation of disordered polylayers. The isotherms of the extended linear compound **2** and the trigonal preorganized amphiphile **3** exhibit comparable monolayer polymorphism.
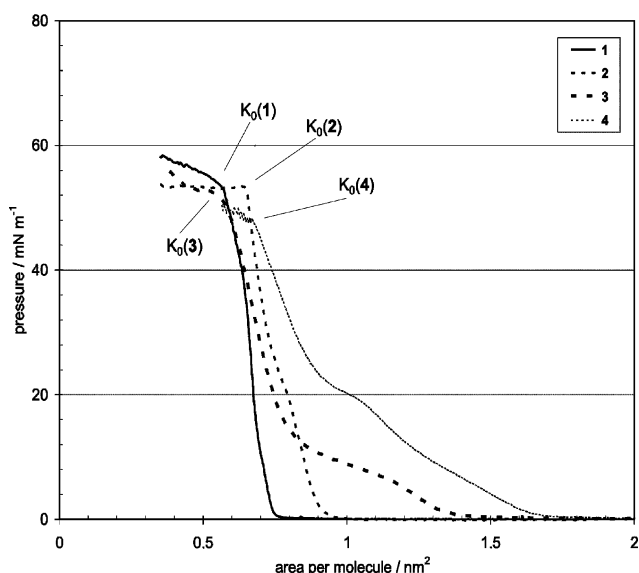
Fig. 2 Isotherms (π–A) of the compounds **1**–**4** on a 10^{-4} M aqueous CaCl$_2$ subphase at 25 °C.

Fig. 3 BAM images during the monolayer compression of the bifunctional compound **1**: (a) transition from the gas analogous to the liquid expanded state, $\pi = 3$ mN m^{-1}; (b) liquid condensed state, $\pi = 8$ mN m^{-1}; (c) solid-condensed state of the monolayer, $\pi = 35$ mN m^{-1}; collapse point of the Langmuir film, $\pi = 45$ mN m^{-1}.

Under the same operating conditions with the tetrafunctional compound **4**, a liquid expanded state (1.5–1 nm^2) can be observed.

The experimental value of the lift-off area and the average required space per molecule (A_0) of the oligofunctional amphiphiles **1**–**4**, compared with calculated data of A_0, based on molecular modelling and assuming a perpendicular arrangement of the alkyl chains for each compound, are summarized in Table 1. A good correlation between the measured and calculated values can be determined for the bifunctional compounds **1** and **2**, whereas for compounds **3** and **4** a moderate and bigger deviation can be observed, respectively. This suggests that the molecules of **3** and **4** in the solid-state monolayer are probably no longer laying flat on the water surface but tend to tilt up in a quasi "edge-on" orientation, which is a known property of aromatic disc-shaped compounds,[28] giving rise to the relatively low average spaces required per molecule which are rather similar to the values for compounds **1** and **2**.

Fig. 2 shows the π–A isotherms of the amphiphilic compounds **1**–**4** on a 10^{-4} molar aqueous CaCl$_2$ subphase. The formation of stable monolayers are also observed under these conditions. Moreover, as follows from Table 1, the presence of the divalent Ca^{2+} ions results in more space required per molecule for all compounds. Obviously, this is due to an increase of the hydrophilic interaction which is supported by the Ca^{2+} ions, leading to enhanced conformational rigidity and favoring a plane or "face-on" arrangement of the amphiphiles at the water surface. In fact, here the data for A_0 given in Table 1 are very close to the calculated areas of the amphiphiles.

The application of the non-resonant Brewster angle microscopy (BAM)[29] is a useful tool for investigation of the morphological texture of the Langmuir film and of the dynamic process of monolayer compression at the air/water interface. The main advantage of BAM is that the morphology of
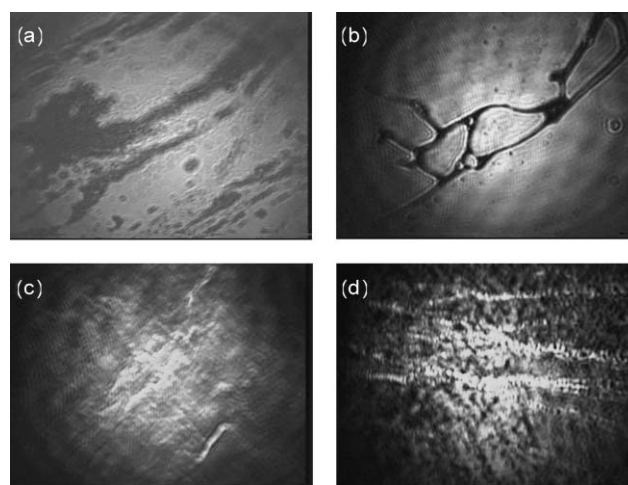
monolayers at the air/water interface can be visualized without affecting the monolayer with probes. Fig. 3 illustrates the BAM images during the compression procedure of the Langmuir film composed of compound **1**. Condensed phase domains are formed directly after the spreading procedure, so that only irregularly shaped condensed phase domains surrounded by the fluid subphase are formed (Fig. 3a). The transition of the monolayer from the gas analogous to the liquid expanded state takes place at a pressure of approximately 3 mN m^{-1}. Up to a pressure of 8 mN m^{-1}, two different morphological states coexist which can be described under thermodynamic considerations as the transition to the liquid condensed state of the monolayer (Fig. 3b). In spite of the nearly closed coverage of the water surface, loose clods and small regions of uncovered subphase can be detected. Further compression of the monolayer leads to the solid–condensed phase where a high degree of homogeneity without inner texture could be detected, and a smooth surface morphology was observed (Fig. 3c). This process is associated with a strong increase in the surface pressure up to 45 mN m^{-1}. Continued compression of the thin film finally leads to the evolution of non-regular morphological patterns due to the increasing lateral pressure. At the collapse point, K_0, the existence of the dense packed monomolecular Langmuir film is terminated and the molecules draw aside in the third dimension, recognizable at the cracks and slips in Fig. 3d.

Langmuir–Blodgett films and AFM characterization

Since the amphiphiles **1**–**4** proved efficient in the formation of stable Langmuir films on a water or on a 10^{-4} M CaCl$_2$ subphase, transfer of the monolayers to a solid support (in order to generate Langmuir–Blodgett type coating films[7,27]) is promising. This was performed by using the 10^{-4} M CaCl$_2$ subphase and freshly cleaved mica plates at a surface pressure of 25 mN m^{-1}. As expected, the transfer of the monolayers **1**–**4** to the hydrophilic mica plate occurs with a dipper speed of

Table 1 Results of the lift-off area (A_0) and calculated minimum area of the compounds **1**–**4** on the water subphase and 10^{-4} molar aqueous CaCl$_2$ subphase

	Water subphase			Subphase 10^{-4} M CaCl$_2$	
Compound	Lift-off area/nm^2	A_0/nm^2	Calculated area/nm^2	Lift-off area/nm^2	A_0/nm^2
1	0.75	0.61	0.62	0.83	0.70
2	0.98	0.73	0.74	1.00	0.79
3	1.04	0.70	0.88	1.46	0.84
4	1.56	0.79	1.12	1.65	1.07

0.5 mm min⁻¹ only by horizontal lifting from the Langmuir films, producing a hydrophobic coating of the support. The transfer ratio was found between 0.99 and 1.19 indicating the effectiveness of the transfer.

For characterization of the surface topography of the transferred monolayers, the tapping mode atomic force microscopy[30] was used. The surface topography of the monofilms composed of the amphiphiles **1** and **3** shows marked differences in the roughness. While the linear amphiphile **1** gives rise to distinct smoothness of the surface, the trigonal amphiphile **3** reveals a rather rough structure, which is in agreement with the property of Langmuir film formation where **1** also yielded a more dense packing in the solid-condensed state compared to **3**. Nevertheless, coating of the mica surface is complete in both cases. Accordingly, the LB-films of compounds **1** and **3** differ in their properties of elasticity, hardness and adhesive strength registered through the phase shift of the oscillating AFM cantilever.

Crystal structure analysis

Although no crystal structures of the amphiphilic target compounds could be obtained because of lacking single crystals, X-ray crystal structures including the functionalized terminal unit **12** and two relevant intermediate compounds (**5a** and **5b**) were successfully determined.‡ The supramolecular hydrogen bond

type interactions involved in these structures are summarized in Table 2.

Crystallization of the diphenolic diester **5a** from dimethyl-sulfoxide yielded a corresponding 1 : 2 solvent complex of the triclinic space group P-1 with one half of the host molecule in the asymmetric unit of the cell. The molecular structure which is illustrated in Fig. 4 shows a deviation of 7.3° of the ethynylene spacers from linearity to give the basic molecule a slightly undulated geometry. The crystal packing is characterized by supramolecular sheets of **5a** and DMSO held together by a close network of hydrogen bonds including different modes of interaction (Fig. 5). The solvent molecules are associated with the hydroxyl groups of **5a** by conventional O–H⋯O hydrogen bonds[31] while one of the less acidic hydrogens of each methyl group of DMSO is connected with the carbonyl oxygen of two adjacent molecules of **5a**. Moreover, weak hydrogen bonds of the C–H⋯O type[32] connect inversion related molecules of **5a**. Due to the unsaturated nature of the backbone of **5a**, π–π stacking interactions[33] dominate between the molecular layers with mean distance between consecutive layers of 3.5 Å involving the interacting aromatic rings.

In the crystal structure of compound **5b** (space group P-1, $Z = 1$), which is equated with the diether derivative of **5a** or the ester analogue of the amphiphile **1**, the unsaturated part of the molecule together with the non-polar dodecyl residues exhibit a nearly planar arrangement showing anti orientation of both the alkyl groups and ester functions relative to each other. Also in the present structure, the molecules establish two-dimensional supramolecular aggregates which are stabilized by van der Waals forces and hydrogen bonding. The particular constitution of
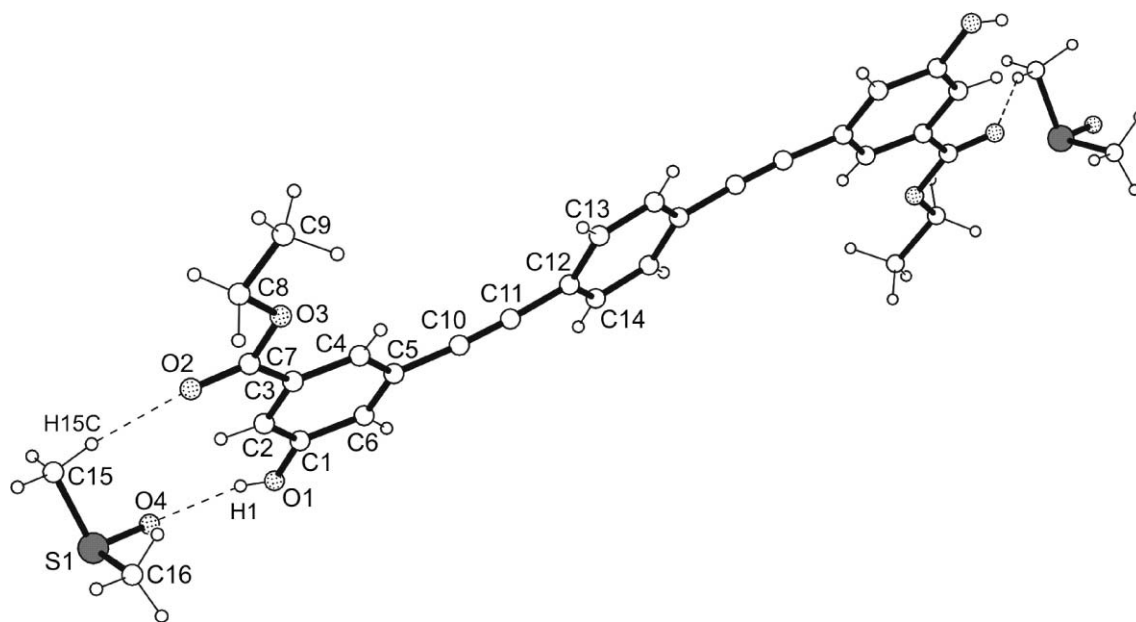

Fig. 4 Molecular structure of **5a**·DMF (1 : 2). H bond type interactions are specified as broken lines.

Table 2 Distances (Å) and angles (°) of hydrogen bond type interactions

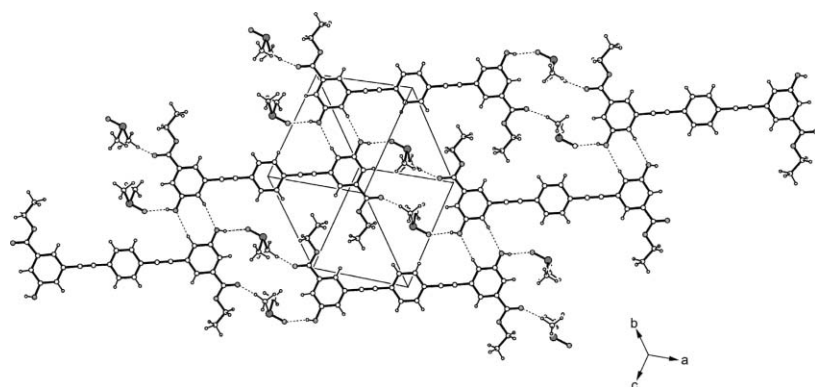| D	H	A	D–H	H⋯A	D⋯A	D–H⋯A	Symmetry
5a							
O1	H1	O4	0.84	1.83	2.662(3)	172	*x, y, z*
C6	H6	O1	0.95	2.52	3.446(3)	164	1 − *x*, 2 − *y*, 1 − *z*
C15	H15C	O2	0.98	2.35	3.251(4)	153	2 − *x*, 1 − *y*, 1 − *z*
C16	H16B	O2	0.98	2.57	3.426(4)	146	2 − *x*, 1 − *y*, 1 − *z*
5a							
C18	H18B	O2	0.98	2.66	3.570(2)	155	2 − *x*, 2 − *y*, −*z*
C25	H25	O3	0.95	2.46	3.370(2)	160	−1 + *x*, 1 + *y*, *z*
12							
O1	H1	O2	0.82	1.91	2.727(3)	175	1/2 − *x*, 1/2 + *y*, 1 − *z*
C11	H11	O1	0.93	2.35	3.271(4)	172	3/2 − *x*, −1/2 + *y*, 2 − *z*

Fig. 5 Packing excerpt of **5a**·DMF (1 : 2) showing the supramolecular layer structure with H bond type interactions given as broken lines.
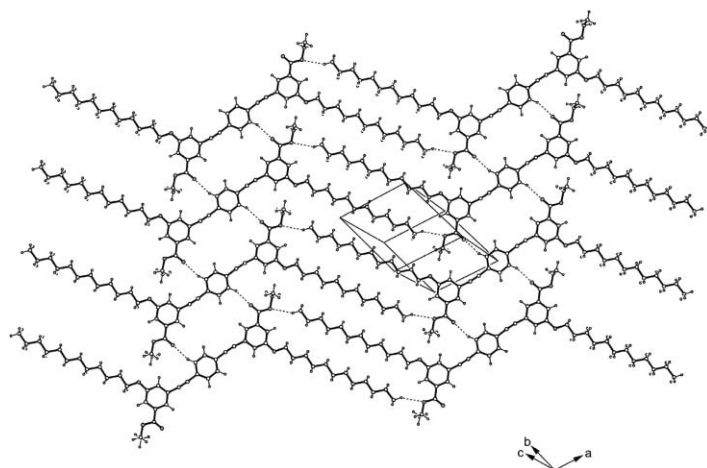

Fig. 6 Packing illustration of **5b** with H bond type interactions specified as broken lines.

5b induces a crystal packing in which hydrophobic domains formed by dodecyl residues alternate with regions established by the tricyclic building blocks of the molecules (Fig. 6). A weak C–H···O contact[32] exists between the carbonyl oxygen and a hydrogen atom of the central arene ring of a symmetry related molecule. Moreover, the distance between the ester alkoxy oxygen and the terminal dodecyl residue of a neighboring molecule indicates an attractive contact to stabilize the packing structure of **5b**.

The phenolic ester **12**, which can be considered as a molecular fragment of **5a**, generates a specific two-dimensional hydrogen bonded aggregate in the crystalline state (Fig. 7). This involves strong intermolecular O–H···O hydrogen bonds[31] between hydroxyl and carbonyl oxygens as well as weaker C–H···O contacts[32] including the ethynyl hydrogen and the phenolic oxygen thus being in H-donor and acceptorship. In contrast
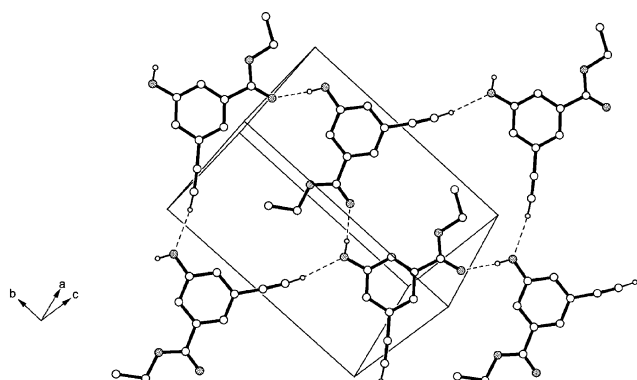
to the above structures, no aromatic stacking interactions[33] are observed in the packing of **12**.

Conclusions

Langmuir and Langmuir–Blodgett (LB) films composed of molecules more complex than the conventional rod-like amphiphiles are clearly expected to display encouraging new properties and structures, having prompted our effort in the field. Thus, stimulated by the so-called "Gemini surfactants"[11] consisting of two or more hydrophilic head groups and hydrophobic aliphatic chains, which have previously been modified by tethering to an aromatic core,[12] and are based on the well-known principle of supramolecular preorganization,[4,10] a new type of oligofunctional amphiphile has been developed and synthesized, represented by compounds **1–4**. They feature a highly rigid and geometrically well-defined central unit composed of ethynylene and attached amphiphilic segment groups, also being of rigid geometry.

This particular design of amphiphilic compounds proved useful in the formation of well-defined Langmuir monolayers on different aqueous subphases that can be transferred to a mica solid support by the LB technique.[6,7] Both the properties of the Langmuir and LB films, including packing behavior and surface topography, depend on the particular molecular structure, as determined by analysis of the π–A isotherms,[26,27] Brewster angle[29] and atomic force microscopy.[30] Thus, our strategy has the potential to provide a controlled two-dimensional surface arrangement of hydrophobic tails and polar heads with desirable geometries and distances owing to the supramolecular preorganization.

Future research will be directed to obtaining even more control over the organization of the self-assembling components by supplying the preorganized amphiphiles with additional

Fig. 7 H-bonded network structure in the packing of **12**. H bonds are given as broken lines.

interacting groups according to the supramolecular synthon approach[34] which is a promising aspect for new applications.

Experimental

General methods

Melting points (uncorrected) were determined with a Kofler melting point microscope (VEB Dresden Analytik). NMR spectra (internal standard TMS, δ in ppm, J in Hz) were recorded on a Bruker Avance DPX 400 at 400.1 (^{1}H) and 100.6 MHz (^{13}C) at room temperature. IR spectra (v in cm^{-1}) were measured on a Perkin Elmer FT-IR 1600. GC-MS spectra were recorded on a Hewlett-Packard (Palo Alto, USA) GC-MS-coupling 5890 Series II/MS 5989A. EI-MS spectra were measured on a Micromass Autospec Q, MADLD-TOF spectra on a Hewlett-Packard G2025A MALDI-TOF-MS system, ESI-TOF spectra on a Mariner ESI-TOF-MS from Applied Biosystems (Weiterstadt, Germany), and the FAB(+)-MS (LSIMS) spectra were accomplished with a Micromass Autospec Q (Switzerland). Elemental analyses were determined with a Heraeus CHN rapid analyzer.

Compounds and materials

The following reagents and compounds were purchased: bibenzyl (Fluka), 1-bromododecane (Fluka), 18-crown-6 (Merck), 1,4-diiodobenzene (Fluka), 3-nitrobenzoic acid (Fluka), orthoperiodic acid (Riedel-de Haën), trimethylsilylacetylene (ABCR), and 1,3,5-tribromobenzene (Fluka). Organic solvents were purified by standard procedures. For column chromatography, silica gel (Merck, 63–100 μm) was used.

1,3,5-Triiodobenzene was prepared from 1,3,5-tribromobenzene with potassium iodide, nickel powder and iodine in DMSO using the literature procedure.[17] Sublimation of the crude product yielded 72% of colorless fine crystals; mp 159–162 °C (lit.[17] mp 163 °C).

1,2,4,5-Tetraiodobenzene was obtained from benzene and periodic acid–potassium iodide in concentrated sulfuric acid according to the literature.[18] Crystallization from pyridine–methanol (1 : 1) yielded 67% of a yellow solid; mp 247–149 °C (lit.[18] mp 249–252 °C).

Bis(4-bromophenyl)acetylene was synthesized by bromination of diphenylethane in water–acetic acid followed by elimination of the dibromo adduct with sodium ethoxide in ethanol.[15,16] Crystallization from chloroform yielded 48% of a colorless solid; mp 184 °C (lit.[16] mp 182–184 °C).

3-Amino-5-bromobenzoic acid was prepared from 3-nitrobenzoic acid by direct bromination and subsequent reduction with Sn–HCl.[19] Crystallization from ethanol yielded 73% solid; mp 222 °C (lit.[19] mp 220–222 °C).

3-Bromo-5-hydroxybenzoic acid (9) was obtained from 3-amino-5-bromobenzoic acid *via* diazotation and hydrolysis.[19] Crystallized from water in the presence of charcoal yielded 86% of a light yellow solid; mp 238 °C (lit.[19] mp 238–239 °C).

Ethyl 3-bromo-5-hydroxybenzoate (10). To a solution of 9 (12.5 g, 57.0 mmol) in anhydrous ethanol (60 mL) conc. H$_2$SO$_4$ (1.5 mL) was added. The reaction mixture was refluxed for 5 h, the solvent evaporated under reduced pressure, and the resulting oily residue poured into water (400 mL). The organic phase was separated and the aqueous phase extracted thrice with diethyl ether (100 mL). The combined organic layers were washed with diluted Na$_2$CO$_3$ (100 mL) and water (100 mL), dried with Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The residue was crystallized from n-heptane to yield 12.5 g (90%) of a white crystalline solid, mp 96 °C.

Ethyl 3-hydroxy-5-[2-(trimethylsilyl)ethynyl]benzoate (11). A solution of 10 (10.0 g, 41.0 mmol) in triethylamine (250 mL) was heated under reflux for 15 min while argon is passed through the solution to keep it free from air. After cooling to room temperature, the catalyst mixture (composed of palladium(II) acetate (60 mg), triphenylphosphane (117 mg) and copper (I) iodide (50 mg)) was added and the solution was heated under reflux for 7 h. During this time, trimethylsilylacetylene (7.5 mL, 53.0 mmol) was slowly added to the boiling reaction mixture. After cooling down to room temperature the precipitated triethylamine hydrobromide was removed by filtration and washed with diethyl ether. The solvent was removed under reduced pressure and the obtained oily residue dissolved in diethyl ether. The mixture was washed with diluted HCl followed by water, dried with Na$_2$SO$_4$ (with the aid of charcoal), filtered over celite and evaporated in vacuum. Purification of the crude product was carried out by stirring with petroleum ether (40–60) to yield 9.1 g (85%) of a light yellow solid, mp 89–90 °C.

Ethyl 3-ethynyl-5-hydroxybenzoate (12). A solution of 11 (9.0 g, 34.0 mmol) and KF·H$_2$O (7.6 g, 100 mmol) in dimethyl sulfoxide (200 mL) and water (2 mL) was stirred at room temperature for 5 h. The reaction mixture was poured into ice cold 6 N HCl (300 mL) and extracted thrice with diethyl ether. The combined organic layers were washed with diluted NaHCO$_3$ solution and water, and dried over Na$_2$SO$_4$. After evaporation of the solvent the crude oily product was purified by crystallization from n-heptane to yield 6.1 g (95%) of a light yellow crystalline solid, mp 129 °C.

Preparation of compounds 5a–8a (General procedure)[14,21]

The corresponding aryl halide was dissolved in diethylamine (iodide) or triethylamine–toluene (bromide). A slight stream of argon is passed through the solution while heating under reflux for 20 min to remove the oxygen. After cooling down to room temperature the mixture of catalyst, being composed of palladium(II) acetate (50.0 mg), triphenylphosphane (117.0 mg) and copper(I) iodide (60.0 mg) was added and the solution heated under reflux for 20 min. The ethynyl-substituted compound 12 dissolved in the respective amine was added dropwise to the reaction mixture, and refluxing was continued for further 7 h until completion of the reaction (monitored by thin layer chromatography). The mixture was allowed to cool down to room temperature and the precipitate (catalyst, di- or triethylamine hydrobromide respectively hydroiodide) was removed by filtration and washed with diethyl ether. The solvent was removed under reduced pressure. Further details and data of the individual compounds are given below.

Diethyl 5,5′-[benzene-1,4-diyl-bis(ethyne-2,1-diyl)]bis(3-hydroxybenzoate) (5a). 1,4-Diiodobenzene (3.30 g, 10.0 mmol), 12 (3.80 g, 20.0 mmol) and the catalyst in diethylamine (100 mL) were used. The crude product was dissolved in THF and treated with charcoal. The solvent was removed in vacuum and the residue taken up with a small amount of acetone. By addition of n-heptane, a light-brown solid precipitated which was purified by column chromatography (SiO$_2$, petroleum ether (40–60)–THF 2 : 1) to obtain 3.7 g (68%) of a white solid, mp 263–265 °C.

Diethyl 5,5′-[tolan-4,4′-diyl-bis(ethyne-2,1-diyl)]bis(3-hydroxybenzoate) (6a). Bis-(4-bromophenyl)acetylene (3.51 g, 10.5 mmol), compound 12 (4.0 g, 21.0 mmol) and the catalyst in triethylamine and toluene (140 mL, 1 : 1) were used. The crude viscous product was stirred with n-heptane to obtain a light-brown solid, which was purified using column chromatography (SiO$_2$, petroleum ether (40–60)–THF, 2 : 1) to yield 4.05 g (70%) of a crystalline solid, mp 197–200 °C.

Triethyl 5,5′,5″-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]-tris(3-hydroxybenzoate) (7a). 1,3,5-Triiodobenzene (2.4 g, 5.25 mmol), compound 12 (3.0 g, 15.75 mmol) and the catalyst in diethylamine (100 mL) were used. Purification was carried out by column chromatography (SiO$_2$, petroleum ether (40–60)–THF, 2 : 1) to yield 2.5 g (74%) of a light yellow solid, mp 153–155 °C.

Tetraethyl 5,5′,5″,5‴-[benzene-1,2,4,5-tetrayl-tetrakis(ethyne-2,1-diyl)]tetrakis(3-hydroxybenzoate) (8a). 1,2,4,5-Tetraiodobenzene (3.05 g, 5.25 mmol), compound **12** (4.0 g, 21.0 mmol) and the catalyst in diethylamine (150 mL) were used. The crude viscous product was dissolved in THF, treated with charcoal and filtered. The resulting yellow solution was slowly added under stirring to the tenfold amount of petroleum ether (40–60) giving rise to precipitate, which was purified by column chromatography (SiO$_2$, petroleum ether (40–60)–THF, 2 : 1) to yield 2.9 g (67%) of a light yellow solid, mp > 260 °C.

Preparation of compounds 5b–8b (General procedure)[23]

The corresponding phenol compound (**5a–8a**), anhydrous K$_2$CO$_3$, 18-crown-6 and 1-bromododecane were dissolved in anhydrous butanone and heated under reflux and under argon for 72 h. After cooling down to room temperature, the solvent was evaporated and the residue extracted into methylene chloride. The solid was filtered off and the filtrate washed with diluted HCl followed by aqueous 1 N NaHCO$_3$ and water, then dried (Na$_2$SO$_4$) and evaporated. Further details and data of the individual compounds are given below.

Diethyl 5,5′-[benzene-1,4-diyl-bis(ethyne-2,1-diyl)]bis(3-dodecyloxybenzoate) (5b). Compound **5a** (2.36 g, 5.2 mmol), 1-bromododecane (3.82 g, 15.0 mmol), anhydrous K$_2$CO$_3$ (2.07 g, 15.0 mmol) and 18-crown-6 (10.0 mg) in anhydrous butanone (50 mL) were used. Purification was achieved by column chromatography (SiO$_2$, methylene chloride–*n*-hexane, 2 : 1) to yield 3.37 g (82%) of a light yellow solid, mp 83–84 °C.

Diethyl 5,5′-[tolan-4,4′-diyl-bis(ethyne-2,1-diyl)]bis(3-dodecyloxybenzoate) (6b). Compound **6a** (2.60 g, 4.7 mmol), 1-bromododecane (3.49 g, 14.0 mmol), anhydrous K$_2$CO$_3$ (1.93 g, 14 mmol) and 18-crown-6 (10 mg) in anhydrous butanone (100 mL) were used. Purification was achieved by column chromatography (SiO$_2$, methylene chloride–*n*-hexane, 2 : 1). The product was taken up with *n*-heptane and mixed with ethanol–water (3 : 1) to separate 3.5 g (84%) of a light yellow solid, mp 75–79 °C.

Triethyl 5,5′,5″-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tris(3-dodecyloxybenzoate) (7b). Compound **7a** (1.50 g, 2.33 mmol), 1-bromododecane (1.78 g, 7.15 mmol), anhydrous K$_2$CO$_3$ (0.99 g, 7.15 mmol) and 18-crown-6 (5 mg) in anhydrous butanone (40 mL) were used. The raw product was purified by column chromatography (SiO$_2$, methylene chloride–*n*-hexane, 2:1) to yield 2.03 g (76%) of a light yellow solid, mp 61–63 °C.

Tetraethyl 5,5′,5″,5‴-[benzene-1,2,4,5-tetrayl-tetrakis(ethyne-2,1-diyl)]tetrakis(3-dodecyloxybenzoate) (8b). Compound **8a** (2.70 g, 3.25 mmol), 1-bromododecane (2.50 g, 10.0 mmol), anhydrous K$_2$CO$_3$ (1.38 g, 10 mmol) and 18-crown-6 (5 mg) in anhydrous butanone (70 mL) were used. The raw product was dissolved in petroleum ether (40–60) and precipitated by addition of ethanol. Further purification was achieved by column chromatography (SiO$_2$, methylene chloride–*n*-hexane, 2 : 1) to yield 3.52 g (72%) of a light yellow solid, mp 62–63 °C.

Preparation of compounds 1–4 (General procedure)[24]

A mixture of the corresponding ethyl ester (**5b–8b**) in ethanol–20% aqueous NaOH (1 : 1) was heated under reflux for 4 h. After cooling down to room temperature, the reaction mixture was filtered and acidified with diluted hydrochloric acid. The resulting white precipitate was collected and washed with water to free from acid. The raw product was dissolved in THF and treated with charcoal which was filtered off. Addition of ethanol–water (1 : 1) yielded a precipitate of the product which was filtered and dried in vacuum. Further details and data of the individual compounds are given below.

5,5′-[Benzene-1,4-diyl-bis(ethyne-2,1-diyl)]bis(3-dodecyloxybenzoic acid) (1). Compound **5b** (2.70 g, 3.25 mmol) and NaOH (5.0 g) in water and ethanol (50 mL, 1 : 1) were used to yield 1.1 g (80%) of a light yellow solid, mp 213–215 °C.

5,5′-[Tolan-4,4′-diyl-bis(ethyne-2,1-diyl)]bis(3-dodecyloxybenzoic acid) (2). Compound **6b** (1.70 g, 1.9 mmol) and NaOH (5.0 g) in water and ethanol (150 mL, 2 : 1) were used to yield 1.27 g (80%) of a light yellow solid, mp 186–190 °C.

5,5′,5″-[Benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tris(3-dodecyloxybenzoic acid) (3). Compound **7b** (1.80 g, 1.6 mmol) and NaOH (5.0 g) in water and ethanol (60 mL, 1 : 5) were used to obtain 1.4 g (82%) of a light yellow solid, mp 186–189 °C.

5,5′,5″,5‴-[Benzene-1,2,4,5-tetrayl-tetrakis(ethyne-2,1-diyl)]-tetrakis(3-dodecyloxy-benzoic acid) (4). Compound **8b** (2.0 g, 1.33 mmol) and NaOH (5 g) in water and ethanol (60 mL, 1 : 5) were used to obtain 1.61 g (87%) of a light yellow solid, mp 250–255 °C.

Langmuir and Langmuir–Blodgett films

A computer-controlled Langmuir film balance system Lauda FW2, equipped with a Wilhelmy platinum plate and a Teflon coated trough was applied. As subphases, pure water, obtained with a Milli-Q-Labo apparatus (18 MΩ cm), as well as a 10^{-4} M aqueous CaCl$_2$ solution were used. The oligofunctional amphiphiles, all prepared in high purity, were at first dissolved in a few drops of DMSO followed by addition of CHCl$_3$ to prepare solutions of concentration of 1 mg ml^{-1}. These solutions were spread on the water surface with a 100 μl micro syringe and by waiting 15 min for solvent evaporation. The monolayers were compressed with a barrier speed of 10 mm min^{-1}. To confirm their reproducibility all isotherms were run at least three times in the direction of increasing pressure with freshly prepared films. The measurements were performed at the constant temperature of 25 °C under clean room conditions.

The Langmuir–Blodgett films on mica plates were performed by transfer of compressed Langmuir monolayers generated on a 10^{-4} M aqueous CaCl$_2$ subphase at a surface pressure of 25 mN m^{-1}. The transfer to the mica substrate was carried out with a dipper-speed of 0.5 mm min^{-1}. The mica plates were freshly cleaved before use in order to ensure a smooth, pure and hydrophilic surface.

Brewster angle microscopy (BAM)

These investigations were carried out using a BAM1 setup from Nanofilm Technologies GmbH with an argon laser illumination source. The images were recorded on a CCD camera and are snapshots of different states of the monolayer recorded upon compression. The lateral resolution was about 4 μm.

AFM measurements

They were accomplished with an Extended Multimode NanoScope IIIa (Digital Instruments, Cambridge, UK) equipped with a silicon cantilever of 125 μm length using the tapping-mode. For topographic and phase imaging determinations the software of Digital Instruments, Version 4.23r3 was applied.

X-Ray diffraction‡

Crystals of **5a** and **5b** suitable for structure analysis were grown by slow isothermal evaporation of solvent from dimethylsulfoxide solutions; crystals of **12** were obtained from chloroform. Compound **5b** crystallizes as trigonal prisms which turned out to be twins.

The intensity data for **5a** and **5b**, collected on a SMART diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) were measured in the ω-scan mode, and for

compound **12** in the ω–2θ scan mode, recorded on a CAD4 diffractometer (graphite monochromated Cu Kα-radiation, $\lambda = 1.5418$ Å). Reflections were corrected for background, Lorentz and polarisation effects. The crystal structures were solved by using direct methods[35,36] and difference Fourier synthesis and refined by full-matrix least-squares.[37] Absorption correction for compounds **5a** and **5b** were performed by using empirical methods, and for **12** the WinGX program[38] was used. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the hydroxyl groups were partly obtained from the difference Fourier map, in other cases included in the models in calculated positions and refined as constrained to bonding atoms.

Acknowledgements

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