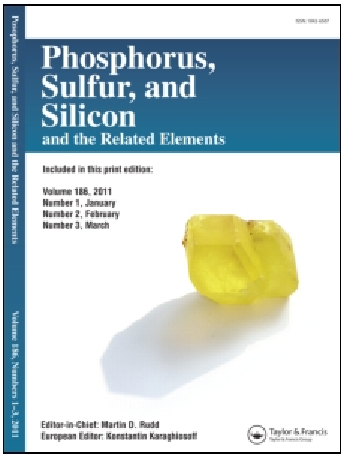

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PREPARATION OF 3-LONG-CHAIN SUBSTITUTED 5-MEMBERED HETEROARYLENES AND STUDIES OF THEIR LANGMUIR-BLODGETT FILM FORMATION

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PREPARATION OF 3-LONG-CHAIN SUBSTITUTED 5-MEMBERED HETEROARYLENES AND STUDIES OF THEIR LANGMUIR-BLODGETT FILM FORMATION

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Dedicated to John Verkade on the occasion of his 60th birthday

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The synthesis of amphiphilic thiophene **1** and pyrrole **5** were achieved via Wittig and Friedel-Crafts reactions respectively. The ability of **1** and **5**, as well as 3-heptadecylthiophene and poly(3-heptadecylthiophene), to form Langmuir-Blodgett films are discussed.

Key words: Langmuir-Blodgett films, thiophene, poly(thiophene), pyrrole.

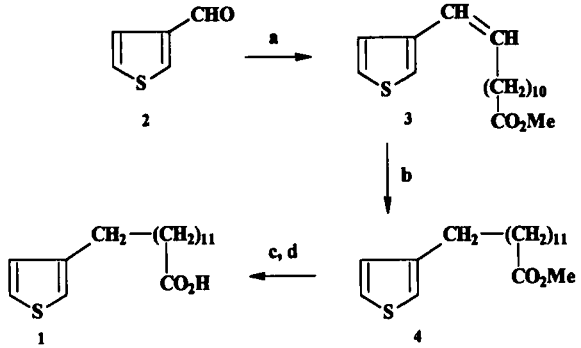
INTRODUCTION

Recently, remarkable progress has been made toward the development of stable, processible electrically conductive polymers.[2–6] Many of the important advances in this area have centered on the design and synthesis of suitably modified monomeric units.[2,7,8]

The Langmuir-Blodgett (LB) technique provides a unique opportunity to fabricate electrically conductive polymers into ultra thin films with well defined molecular organization.[9,10] Here we report the synthesis of hitherto unknown amphiphilic thiophenes **1** and pyrroles **5** as potential molecular architects capable of forming monolayer films via the LB technique. Polymerization of such well arranged molecules could be achieved chemically as well as electrochemically, leading to a highly ordered polymer system. Toward that goal, the ability of **1** and **5** to form LB films is presented along with similar investigations of 3-heptadecylthiophene (**10**) and poly(3-heptadecylthiophene) (**11**).

RESULTS AND DISCUSSION

The synthesis of 13-(3-thienyl)-*n*-tridecanoic acid **1** was achieved following the stepwise procedures shown in Scheme I. Thus, reacting thiophene-3-carboxaldehyde (**2**) with methyl *n*-dodecanoate-12-yl-phosphonium bromide in the presence of *n*-butyllithium afforded cis/trans methyl 13-(3-thienyl)-12-tridecenoate (**3**) in good yield. Reduction of **3** to 13-(3-thienyl)-*n*-tridecanoate (**4**) was accomplished by catalytic hydrogenation using 5% Pd/C under 40 psi of hydrogen gas. Hydrolysis of **3** under basic catalytic conditions furnished **1**. The structure of **1** was confirmed by ^{1}H-NMR and elemental analysis.

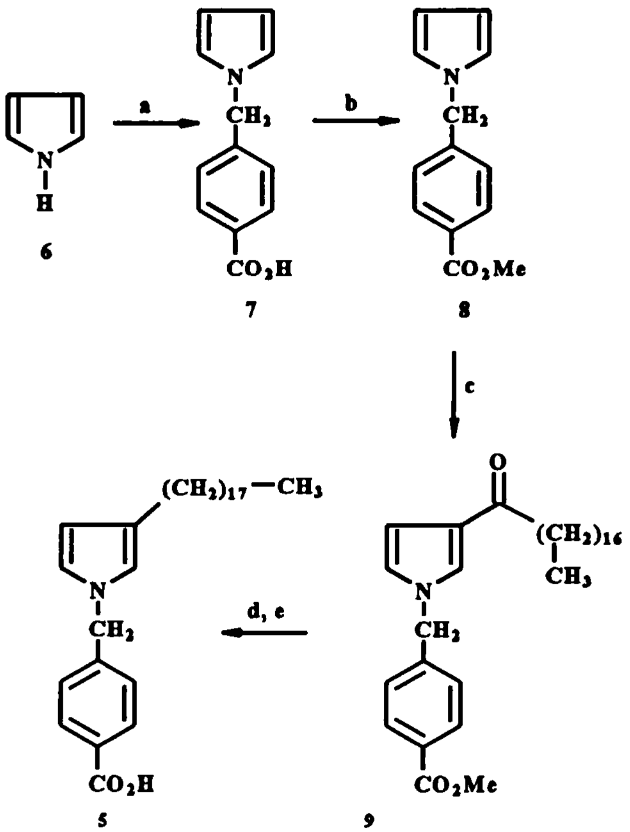


Scheme I a) $Ph_3\overset{\oplus}{P}—(CH_2)_{11}—CO_2Me$ $\overset{\ominus}{Br}$, *n*-BuLi, THF 0°C; b) H_2, Pd/C; c) 10% NaOH, Δ; d) 1 N HCl

The construction of (3-octadecyl-N-pyrrolomethyl)benzoic acid (**5**) involved the stepwise procedures shown in Scheme II. Thus, coupling the sodium salt of the pyrrole **6** with *p*-bromomethylbenzoic acid in dry dimethylformamide afforded 4-N-pyrrolomethylbenzoic acid (**7**). Protection of the carboxyl group by methylation using dimethyl sulfate, followed by acylation of the resulting methyl ester **8** using tin (IV) chloride as a catalyst, led to the formation of the 3-octadecanoyl isomer **9** as a major product. Purification of **9** by flash chromatography, followed by reduction and hydrolysis, afforded **5**.

Compounds **1**, **5**, and 3-heptadecylthiophene[7] (**10**), as well as poly(3-heptadecylthiophene)[11] (**11**), were tested for their ability to form Langmuir-Blodgett films on subphases of pure water and 10^{-3} M cadmium chloride. In Table I, the collapse pressures (mNm^{-1}) and co-areas ($nm^2molecule^{-1}$) are listed. Compound **1** exhibited no film forming capability on a pure water subphase. On a cadmium chloride subphase, a collapse pressure of 13 mNm^{-1} with a co-area of 0.13 $nm^2molecule^{-1}$ was determined as indicated on its surface pressure-area (π-A) isotherm, Figure 1. This low value for the co-area may indicate solubility of the monolayer in the subphase due to the relatively short carbon chain.

On a pure water subphase, **5** had a collapse pressure of 40 mNm^{-1} with a co-area of 0.36 $nm^2molecule^{-1}$. Use of a cadmium chloride subphase increased the collapse pressure to over 50 mNm^{-1} while lowering the co-area to 0.33 $nm^2molecule^{-1}$. Initial compressive creep tests indicated good stability for the first thirty minutes with a slow creep to 90% of the original area over the next two hours. Methylation of the carboxyl group on **5** destroyed its film forming ability, indicating the importance of



SCHEME II a) NaH, p-HOOC-C_6H_4-CH_2Br, DMF; b) DMS, K_2CO_3,$(CH_3)_2CO$; c) ClC(O)-$(CH_2)_{16}$-CH_3, $SnCl_4$; d) NH_2NH_2, KOH, HO-$(CH_2)_2$-OH, Δ; e) 1 N HCl.

TABLE I

Collapse pressures and co-areas for 3-long-chain substituted thiophene and pyrrole based materials

Compound	Subphase	Collapse Pressure mN m-1	Co-area nm^2 molecule-1
1	Water	--	--
1	Cadmium Chloride	13	0.13
5	Water	40	0.36
5	Cadmium Chloride	50	0.33
10	Water	--	--
10	Cadmium Chloride	--	--
11	Water	60	0.12
11	Cadmium Chloride	60	0.12

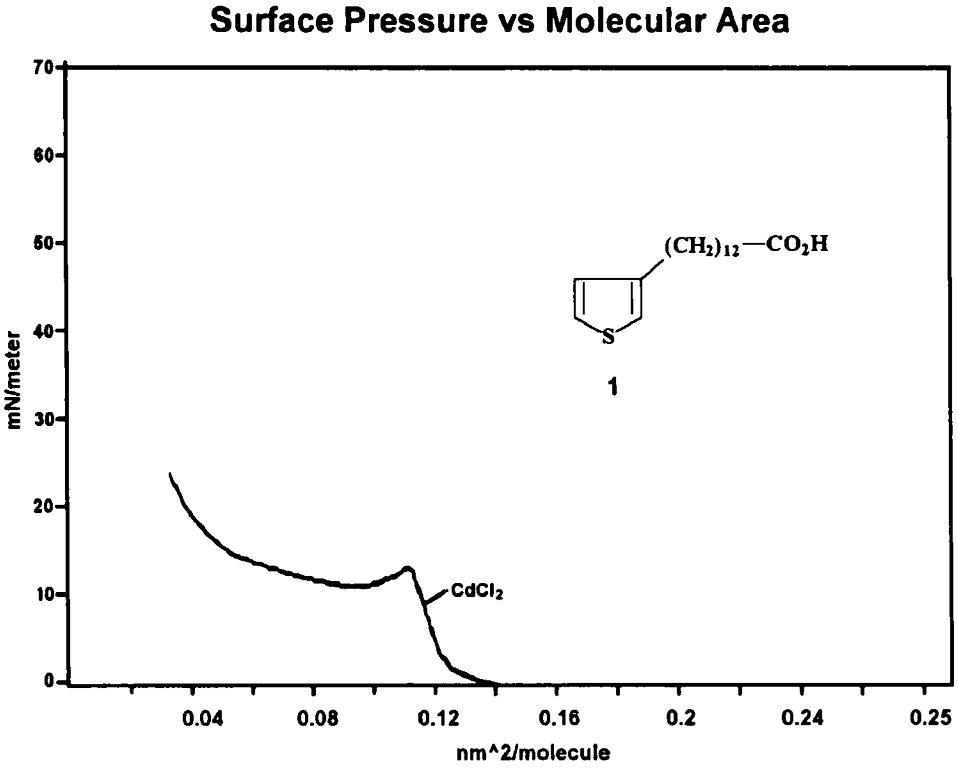


FIGURE 1 Surface pressure-area (π-A) isotherm of **1**.

the hydrophilic carboxylic acid group to the film forming ability, Figure 2. It is clear that the formation of the cadmium salt of compound **5** has a marked effect on the packing of this monolayer at the gas-water interface. This data indicates that the formation of good polymerized monolayers based on this type of pyrrole monomer unit is probable, and that transfer by the Langmuir-Blodgett technique to form ordered multilayers of this polymer is likely.

Compound **10** gave surface pressure values too low for monolayer formation, Figure 3. A monolayer does not form due to the lack of a hydrophilic group. The interaction of the water's surface with the thiophene moiety was not strong enough to allow monolayer formation. This material exhibits liquid like behavior.

Compound **11**, which is the chloroform soluble electropolymerized form of **10**, gave a high modulus isotherm with a collapse pressure of 50 mNm^{-1} and a low co-area of 0.12 $nm^2molecule^{-1}$. The monolayer characteristics were unaffected by using cadmium chloride as a subphase. The low co-area may be attributed to the non-adherence of some of the monolayer units to the subphase, which should result in thicker layers and an apparently low co-area. This was verified to some extent by ellipsometry measurements giving an average thickness 50% greater than expected from the length of the side chain. Also it is possible that a tilted bilayer structure could be responsible for the low apparent co-area. Characterization of Langmuir-Blodgett multilayers from this polymer layer should answer questions about the structure present at the gas-water interface.

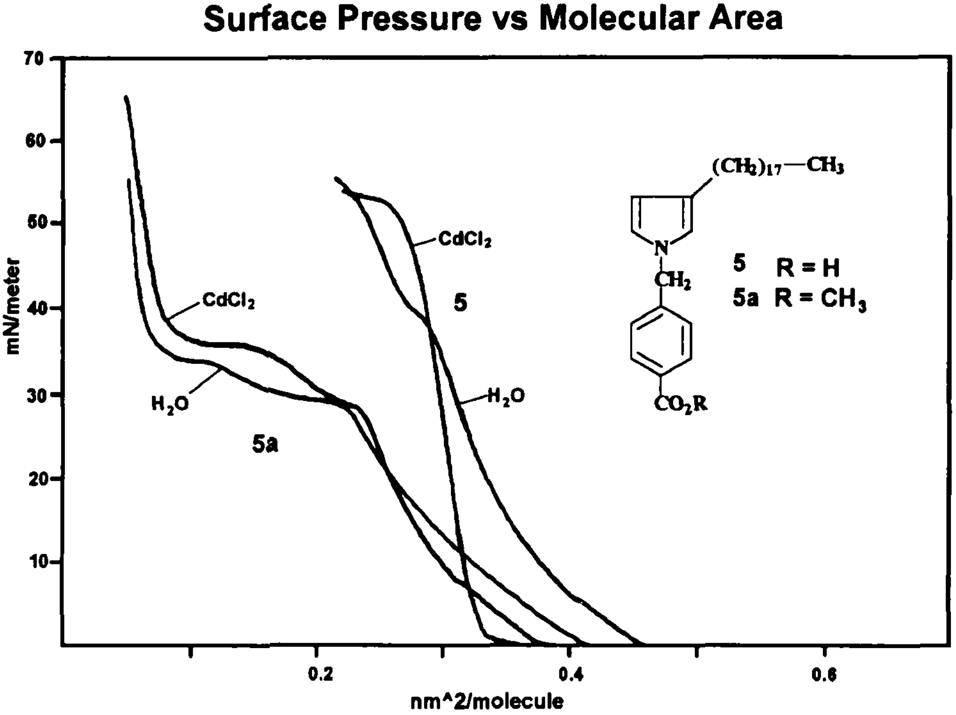


FIGURE 2 Surface pressure-area (π-A) isotherm of **5**.

EXPERIMENTAL

Melting points were determined with a Mel Temp apparatus and are uncorrected. ^{1}H-NMR spectra were recorded at 80 MHZ and/or 250 MHZ on an IBM, FTQ and Brucker spectrometers, respectively. Chemical shifts are expressed in δ (ppm) relative to tetramethylsilane as the internal standard. Mass spectra were obtained on a Hewlett-Packard 5995 GC-MS spectrometer at 70 eV. Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona. Compounds **10** and **11** were prepared as previously reported.[7,11]

cis/trans Methyl 13-(3-thienyl)-12-tridecenoate (**3**): In a dry, three-necked flask under a dry nitrogen atmosphere, 32 g (58 mmol) of dry methyl *n*-dodecanoate-12-yl-triphenylphosphonium bromide was dissolved in 300 ml of dry tetrahydrofuran. The mixture was cooled to 0°C and 47 ml of 1.2 M *n*-butyllithium was added over 10 minutes and stirring continued for 0.5 hour. Then, 6.5 g (58 mmol) of thiophene-3-carboxaldehyde was added. After stirring overnight, the solvent was removed via distillation under reduced pressure. The remaining residue was crushed in 50 ml of 0.1 N sodium chloride and extracted with diethyl ether (2 × 75 ml). The ether extracts were combined and dried over anhydrous magnesium sulfate. After distilling off the ether under reduced pressure, the crude residue was purifed via column chromatography (silica gel) using petroleum ether (35–60°C) as eluent: yield 70% ^{1}H-NMR (80 MHZ, $CDCl_3$) δ 7.23 (1H, s), 6.92 (2H, d), 6.3 (1H, m), 5.6 (1H, m), 3.7 (3H, s), 3.52 (2H, t), 2.3 (2H, t), 1.2 (16H, bs+m). Anal. Calcd. for $C_{18}H_{28}O_2S$: C, 70.08, H, 9.15; found: C, 69.89; H, 9.24.

Methyl 13-(3-thienyl)-n-tridecanoate (**4**): In a Parr apparatus, 2 g (65 mmol) of cis/trans methyl 13-(3-thienyl)-12 tridecenoate was dissolved into 75 ml of ethyl acetate. To this mixture, 0.5 g of 5% palladium on carbon catalyst was added. The mixture was put under hydrogen at 40 psi and shaken for 6 hours. The resulting mixture was filtered and the filtrate was dried over anhydrous magnesium sulfate. Removal of the solvent afforded an oily residue which was further purified by a bulb to bulb distillation, yield *nearly quantitative*. ^{1}H-NMR (250 MHZ, $CDCl_3$) δ 7.23 (1H, m), 6.92 (2H, d), 3.65 (3H, s), 2.61 (2H, t), 2.97 (2H, t), 1.61 (4H, m), 1.25 (16H, bs+m). Anal. Calcd. for $C_{18}H_{30}O_2S$: C, 69.63; H, 9.74; found: C, 69.63; H, 9.77.

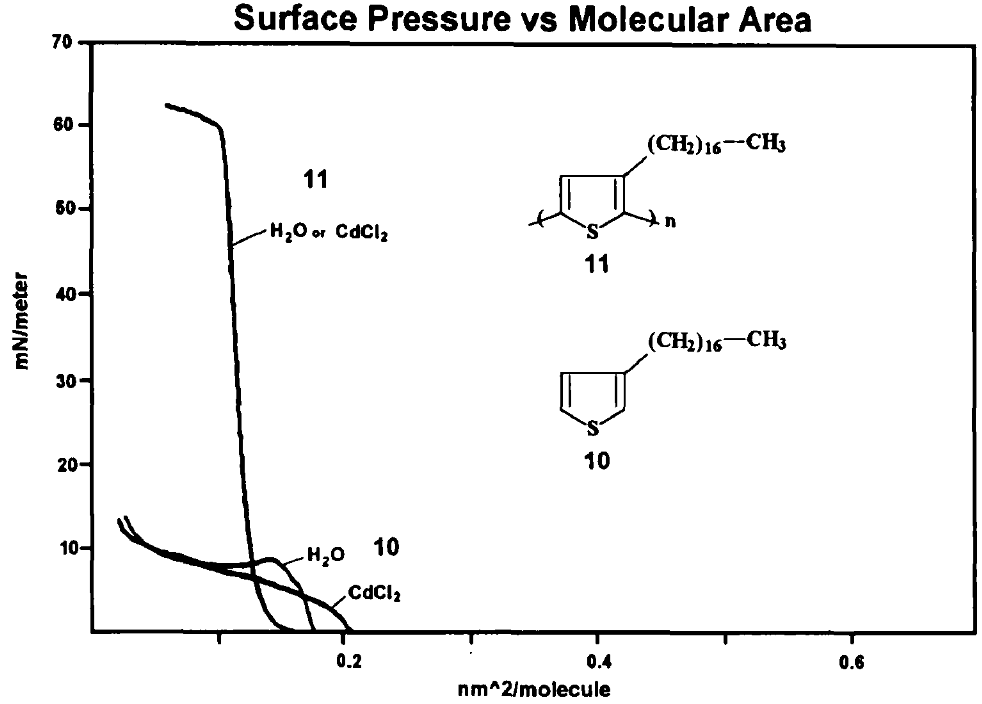


FIGURE 3 Surface pressure-area (π-A) isotherm of **10** and **11**.

13-(3-Thienyl)-n-tridecanoic acid (**1**): In a round-bottom flask, 2 g (6.5 mmol) of methyl 13-(3-thienyl)-*n*-tridecanoate was dissolved into 30 ml of 10% sodium hydroxide. The mixture was refluxed for 1–2 hours, cooled to room temperature, and acidified with 1 N hydrochloric acid. The aqueous solution was then extracted with chloroform (2 × 50 ml). The chloroform layers were combined and dried over anhydrous magnesium sulfate. The chloroform was removed via distillation under reduced pressure; yield 65%, (mp 67–68°C); MS (EI): m/z 296 (M^{+}, relative intensity 3%), 111 (11), 98 (40), 44 (20). Anal. Calcd. for $C_{17}H_{28}O_2S$: C, 68.87; H, 9.52; found: C, 68.76; H, 9.41.

4-N-Pyrrolomethylbenzoic acid (**7**): In a dry, three-necked flask under a dry nitrogen atmosphere, an amount of 0.46 g (20 mmol) of sodium hydride (0.76 g of 58% dispersion in mineral oil) was washed twice with 10 ml portions of hexane. After washing, 100 ml of dry dimethyl formamide was added. To this stirring suspension, 1.34 g (20 mmol) of pyrrole was added dropwise. After stirring for two additional hours, 2.15 g (10 mmol) of *p*-bromobenzoic acid was added at once and kept overnight. With external cooling, 50 ml of 1 N hydrochloric acid was added dropwise, followed by extraction (3 × 100 ml) with ethyl acetate. The combined organic layers were washed with 0.1 N sodium chloride and dried over anhydrous magnesium sulfate. The solvent was removed via distillation under reduced pressure. The remaining residue (55%) was used directly for the next synthetic step. ^{1}H-NMR (250 MHZ, $CDCl_3$) δ 10.11 (1H, bs), 8.02 (2H, d, $J = 7.5$ Hz), 7.16 (2H, d, $J = 7.5$ Hz), 6.69 (2H, d, $J = 2.5$ Hz), 6.62 (2H, d, $J = 2.5$ Hz), 5.14 (2H, s); MS (EI): m/z 201 (M^{+}, relative intensity 1.5%), 136 (33), 91 (7), 75 (100).

Methyl 4-N-pyrrolomethylbenzoate (**8**): In a dry, three-necked flask under a dry nitrogen atmosphere, 1.53 g (76 mmol) of N-methylpyrrole-*p*-benzoic acid was dissolved into 100 ml of anhydrous acetone. To this mixture, 1.14 g (9 mmol) of dimethyl sulfate and 1.26 g (9 mmol) of potassium carbonate were added and the solution was refluxed for 5 hours. After cooling, a precipitate was filtered off, the solvent removed via distillation under reduced pressure to give a nearly quantitative yield of the methyl ester. The material was used directly for the next synthetic step without further purification. ^{1}H-NMR (250 MHZ, $CDCl_3$) δ 7.96 (2H, d, $J = 7.5$ Hz), 7.11 (2H, d, $J = 7.5$ Hz), 6.67 (2H, d, $J = 2$ Hz), 6.20 (2H, d, $J = 2$ Hz), 5.10 (2H, s), 3.88 (3H, s).

Methyl 4-(3-octadecanoyl-N-pyrrolomethyl)benzoate (**9**): In a dry, round-bottom flask, 1.64 g (7.6 mmol) a solution of methyl 1-N-pyrrolomethylbenzoate in 80 ml of dry benzene was cooled to 0°C, then 3.4 g (11.2 mmol) of octadecanoyl chloride and 1.5 g (85 mmol) of anhydrous tin (IV) chloride over 1 hour with stirring were added. After stirring for 1 hour, 50 ml of 1 N hydrochloric acid were added dropwise. The mixture was then extracted with ethyl acetate (2 × 75 ml). The organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was removed via distillation under reduced pressure. Flash silica gel column chromatography using ethyl acetate:hexane 1:1 gave 1.95 g (53%) of the 3-substituted ketone. ^{1}H-NMR (250 MHZ, $CDCl_3$) δ 7.95 (2H, d, J = 8.1 Hz), 7.09 (2H, d, J = 8.1 Hz), 7.03 (1H, m), 6.92 (1H, bs), 6.22 (1H, m), 5.63 (2H, s), 3.88 (3H, s), 2.72 (2H, t, J = 7.4 Hz), 1.60 (2H, m), 1.25 (28H, bs), 0.87 (3H, t, J = 6.5 Hz); MS (EI): m/z 481 ($M^{+\cdot}$, relative intensity 8%), 284 (17), 257 (100), 242 (25), 149 (36).

3-Octadecyl-N-pyrrolomethyl)benzoic acid (**5**): A mixture of 1 g (2.08 mmol) of methyl 4-(3-octadecanoyl-N-pyrrolomethyl)benzoate dissolved in 100 ml diethylene glycol, 2 g of potassium hydroxide and 0.84 g (10 mmol) of 40% aqueous hydrazine were refluxed for 1 hour when the excess hydrazine was distilled off. After cooling, 50 ml of 1 N hydrochloric acid was added dropwise, followed by an extraction with ethyl acetate (2 × 50 ml). The combined organic layers were washed with 0.1 M sodium chloride and dried over anhydrous magnesium sulfate. The solvent was removed via distillation under reduced pressure. Flash silica gel chromatography using ethyl acetate:hexane 1:1 gave colorless crystals, (mp 97–99°C), yield (56%). ^{1}H-NMR (250 MHZ, $CDCl_3$) δ 10.87 (1H, s), 8.04 (2H, d, J = 7.7 Hz), 7.04 (2H, d, J = 7.7 Hz), 6.16 (1H, m), 6.62 (1H, m), 5.98 (1H, m), 5.11 (2H, s), 2.39 (2H, t, J = 7.5 Hz), 1.54 (2H, m), 1.24 (30H, m), 0.87 (3H, t, J = 7.5 Hz); ^{13}C-NMR (62.5 MHZ, $CDCl_3$, decoupled) δ 171.85, 144.87, 133.63, 130.62, 128.42, 126.15, 120.71, 107.47, 106.17, 49.93, 31.89, 29.67, 29.54, 29.37, 28.73, 26.12, 22.6, 14.1; IR (KBr pellet): cm^{-1} 3019, 2925, 2851, 1693. Anal. Calcd. for $C_{30}H_{47}NO_2$: C, 79.42, H, 10.44; found: C, 79.47, H, 10.51.

LB FILM PREPARATION

Each material was tested for its ability to form a Langmuir-Blodgett film on subphases of pure water and 10^{-3} M cadmium chloride. In Table I, the collapse pressure (mNm^{-1}) and co-area's ($nm^2molecule^{-1}$) are listed. The films were spread from the chloroform solutions of the compounds upon a water subphase. The water used for the subphases was produced using a combination system of Millipore© and Milli-RO© water system in combination with Milli-Q Plus© system. The resulting water had a resistance of approximately 18.2 MΩ cm prior to use. The L-B trough system was equipped with a MGW-Lauda Filmwaage system. The trough rested upon a Kinetic Systems© Vibraplane© air suspension table. For data collection, the PML software library version 3.1^{+}© was used. The employed cadmium chloride subphase had a concentration of 0.001 M and was adjusted to pH 5. It was obtained by adding 23 drops of standardized 0.1 M sodium hydroxide to 0.1833 g of anhydrous cadmium chloride and diluted to 1 liter using the ultra pure water previously described.

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