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A systematic study of thiophene Langmuir–Blodgett films including new conjugated donor–acceptor molecules

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Hemicyanine dyes are an extensively investigated group of materials which show promise for second-order non-linear optical properties; they have also proved to be good materials for deposition by the Langmuir–Blodgett technique. This work concerns a closely related group of materials which contain a thiophene moiety in place of the nitrogen heterocycle of the hemicyanine material. The synthesis of several groups of novel amphiphiles containing the thiophene moiety, and their subsequent screening as materials for deposition by the Langmuir–Blodgett technique is described. General trends in the behaviour of the simplest materials are noted, whilst the report of the characterization of the more complex D–π–A thiophenes is extended to include data relating to the production of heterogeneous monolayer and alternate layer structures.

1. Introduction

Over recent years there has been a great increase in research into Langmuir–Blodgett (LB) thin films, as the LB method is an organic fabrication technique appropriate for the formation of monolayers and multilayers that have a high degree of anisotropy and structural order as well as a precise and uniform thickness [1]. In particular, considerable interest in the second-order non-linear optical properties of molecules that can be deposited as LB films has arisen, because the technique enables them to be readily assembled into non-centrosymmetric structures that ensure that the individual second-order molecular hyperpolarizabilities do not cancel one another [2].

One group of materials that have been investigated extensively [3–5] and which have produced exciting results are hemicyanine dyes, which have a D–π–A system (donor and acceptor groups linked by a conjugated π system) containing a stilbene unit bonded to a heterocyclic group containing nitrogen. In this study a thiophene moiety was incorporated into the molecules in place of the nitrogen heterocycle. The inclusion of a π-excessive centre into a stilbene-type molecule of this type may enhance the second-order non-linear optical properties of the material. Background experiments were performed in which thiophene units were incorporated into various simple long-chain molecules, in order to establish how this moiety was likely to affect the stability of the monolayer at the air/water interface and its transfer ratio on to solid substrates.

2. Experimental procedure

The structures of the series of compounds studied are shown below (Fig. 1). Compounds 1–4 were prepared by conventional methods [6–10], and were then purified via recrystallization and sublimation. An account of the synthetic approaches adopted in the production of the more novel compounds 5a–e is given later, beginning with a reaction scheme (Fig. 2). It includes a convenient process for the separation of the 2-nitrothiophene and 3-nitrothiophene formed on nitration of thiophene. Of the series 5 compounds, only 5e was studied in depth, because the others in this group did not form sufficiently stable monolayers at the air/water interface.

2.1. Preparation of 1-(*N*-alkyl-5′-acetamido-2′-thienyl)-2-(4″-nitrophenyl)-ethene (compounds 5 a–e).

2.1.1. Preparation of 2-acetylamidothiophene

2.1.1.1. Nitration and purification of thiophene. Thiophene (84 g, 1.0 mol) was nitrated by Hartough's method [11]. The resulting mixture of 2-nitrothiophene and 3-nitrothiophene was separated by treating it with chlorosulphonic acid. This gives the water-soluble 5-sulphonic acid from the 3-isomer, and does not react with 2-nitrothiophene. The product from the nitration of thiophene was dissolved in dichloromethane and cooled to 0°C. Chlorosulphonic acid (30 g, 0.26 mol) (approximately 25 mol %) was added dropwise and the solution was stirred for a further 30 min at room temperature, then cautiously added to an equal volume of ice/water. The aqueous layer was further extracted with dichloromethane and the combined organic phases were washed with water, sodium hydrogen carbonate (three times) and then water. Evaporation of the dried solution left pure 2-nitrothiophene; melting point 43–45°C, yield 105 g, 81%.

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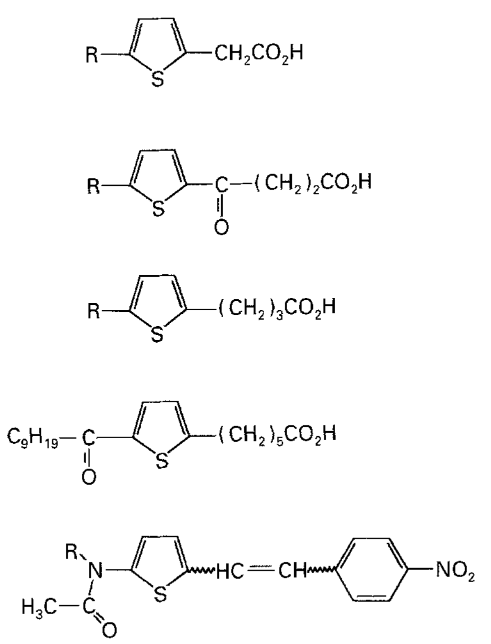

Figure 1 Compounds synthesized for the study: (a) -R = $C_{14}H_{29}$; (b) -R = $C_{16}H_{33}$; (c) -R = $C_{17}H_{35}$; (d) -R = $C_{18}H_{37}$; (e) -R = $C_{22}H_{45}$.

2.1.1.2. Reductive acetylation of 2-nitrothiophene. A solution of 2-nitrothiophene (51.6 g, 0.400 mol) in acetic anhydride (90 g, 0.88 mol) and acetic acid (144 g, 2.40 mol) was stirred with an overhead stirrer and heated to 55–60°C. Once the reaction mixture had attained that temperature, the source of heat was removed and reduced iron (67.2 g, 1.20 mol) was added in small portions. The temperature of the mixture rose after each addition of iron, and it was allowed to fall to 55–60°C before further additions were made. When all the iron had been added, the reaction mixture was heated to 60–70°C and stirred for a further 45 min, then cooled, poured into 2M-hydrochloric acid (approximately an equal volume to the reaction mixture) and left to stand overnight. The mixture was filtered, and the precipitate was dissolved in ethyl acetate. The aqueous layer was washed with ethyl acetate and the combined organic layers were washed with water, sodium hydrogen carbonate (four times) and then water, then dried ($MgSO_4$) and evaporated. The product 2-acetylamidothiophene was crystallized from 1:1 petroleum ether 60–80% ethyl acetate; melting point 167°C, yield 93%.

2.1.2. Preparation of N-alkylated 2-acetamidothiophene [12]

A mixture of 2-acetamidothiophene (7.10 g, 0.05 mol), finely powdered sodium hydroxide (7.0 g, 0.18 mol), potassium carbonate (14.0 g, 0.101 mol), meristyltrimethylammonium bromide (1.70 g, 0.075 mol) and benzene (50 ml) was heated under reflux and with efficient overhead stirring. A solution of *n*-alkylbromide (0.075 mol) in benzene (10 ml) was then added dropwise to the mixture, which was heated under reflux for a further 5 h after the addition was complete. The solution was cooled, diluted with benzene and washed with water several times, dried ($MgSO_4$), and then evaporated. The resulting solid *N*-alkyl-2-acetamidothiophene was purified by column chromatography on silica using dichloromethane as the solvent; yield 43%–73%.

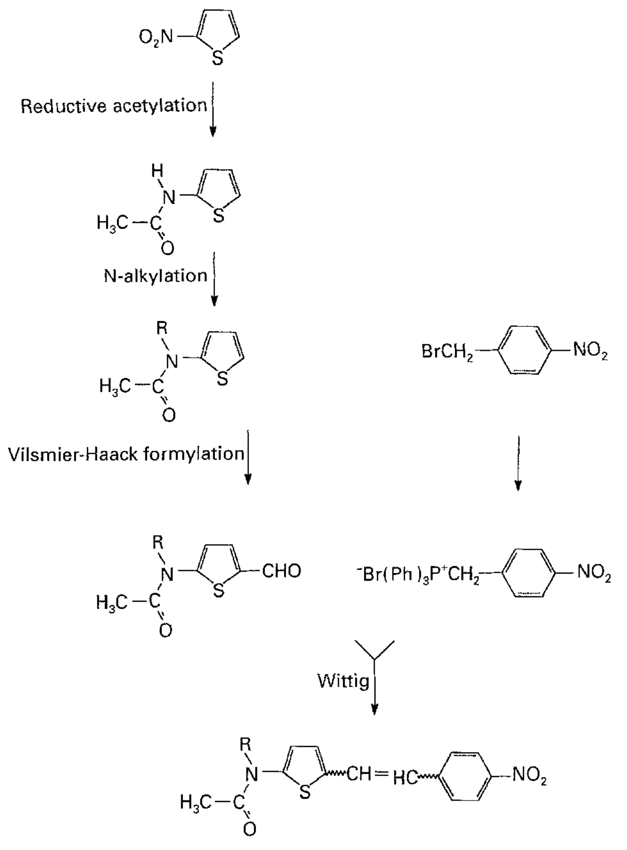

Figure 2 Synthesis route for compounds 5a–e: (a) -R = $C_{14}H_{29}$; (b) -R = $C_{16}H_{33}$; (c) -R = $C_{17}H_{35}$; (d) -R = $C_{18}H_{37}$; (e) -R = $C_{22}H_{45}$.

2.1.3. Formylation of N-alkyl-2-acetamidothiophene [13]

A mixture of *N*-alkyl-2-acetamidothiophene (5.09×10^{-3} mol), *N*, *N*-dimethylformamide (0.47 g, 6.4×10^{-3} mol) and phosphoryl chloride (0.98 g, 6.4×10^{-3} mol) in dry 1,2-dichloroethane (10 ml) was stirred at room temperature for 14 h. The mixture was then poured on to crushed ice and neutralized to pH 6.0–7.0 with anhydrous sodium acetate. The crude product *N*-alkyl-2-acetamidothiophene-5-carboxaldehyde was then purified by column chromatography using chloroform as the elutant; yield 43%–91%.

2.1.4. Synthesis of the triphenylphosphine salt of 4-nitrobenzylbromide [14]

Triphenylphosphine (10.0 g, 0.038 mol) and 4-nitrobenzylbromide (5.00 g, 0.023 mol) in *o*-dichlorobenzene (20 ml) was refluxed gently for 5 min. The mixture was cooled to room temperature and diluted with ether and the solid product was filtered off, washed with dry ether, and then dried in a vacuum desiccator; yield 97%.

2.1.5. Wittig reaction

Butyl lithium (2.4 ml, 1.6 M in hexane) was added to a stirred solution of dry tetrahydrofuran (20 ml) and

4-nitrobenzyltriphenylphosphine bromide (1.70 g, 3.56×10^{-3} mol) at 0° C under a dry nitrogen atmosphere. After all the butyl lithium had been added, the solution was stirred at room temperature until all the triphenylphosphine salt had reacted. Then a solution of *N*-alkyl-2-acetamidothiophene-5-carboxaldehyde (2.38 mol) in dry tetrahydrofuran, was added quickly and the mixture was stirred at room temperature for a further 1 h or until all the *N*-alkyl-2-acetamidothiophene-5-carboxaldehyde had reacted (TLC). The mixture was then poured into water, extracted with chloroform, and the organic layer separated and washed several times with water, then dried ($MgSO_4$), filtered and evaporated to dryness. The resulting crude product (compounds 5a–e in Fig. 1) was then chromatographed on silica 1:1 chloroform/petroleum ether; boiling point 60–80° C; yield 60%–67%.

The identities of all products were confirmed by infrared spectroscopy, ^1H and ^{13}C nuclear magnetic resonance spectroscopies and microanalysis of carbon, hydrogen and nitrogen.

2.2. Langmuir–Blodgett deposition

LB screening and deposition was performed using a commercial Nima Technology trough. In all the experiments the conditions and procedures were identical, with the only variable being the pH of the subphase. Spreading solutions were formed by dissolving the compounds in ARISTAR grade chloroform at a concentration of approximately 1 mg ml^{-1}. Cadmium chloride was added to the subphase to give an approximately 2×10^{-4} M solution; its pH was then adjusted to the required value with hydrochloric acid and sodium hydroxide. The subphase temperature was maintained at 18–20° C. After spreading, each monolayer was allowed a 5 min period for chloroform evaporation prior to compression.

The area per molecule for each material was determined from the isotherms obtained by compressing monolayers at a constant rate of around 50 cm^2 s^{-1}. An appropriate surface pressure for determining monolayer stability as a function of time for each material was chosen to be approximately half way up the steepest part of the graph. Monolayers were maintained at these pressures in order that the rate of loss of monolayer area due to either dissolution into the subphase or collapse of the film could be investigated. Approximate decay-rate figures (Table I) were calculated by finding the gradient of the linear region of a plot of monolayer area against time, ignoring the initial exponential decay region. Using the optimum conditions, the transfer of monolayers to a silicon substrate was investigated at various dipping speeds. When calculating the transfer ratios, the results of the monolayer stability studies were employed in order to make an appropriate allowance for the decay in monolayer area that would have occurred during the period of the dip.

3. Results and discussion

Table I summarizes the results obtained for the simple amphiphilic thiophenes that were prepared. For each individual molecule it can be seen that the pH of the subphase has very little effect on the area per molecule. It is observed that the area per molecule for molecules in group two are larger than those in groups one and three. This is a consequence of the carbonyl group next to the thiophene moiety in the group two molecules preventing them from packing as close together as those in groups one and three.

It can be seen from the decay rates that the longer the hydrophobic hydrocarbon "tail" the more stable the molecules are to dissolution or collapse; furthermore, the molecules in group two are less stable than those of a corresponding length in group three. This is again probably due to the lower packing density, and hence reduced intermolecular interactions. When comparing molecules of the same overall length but with the thiophene moiety in a different position along the carbon chain (cf. 3b with 1d), it can be seen that there is very little difference in monolayer stability.

TABLE I Langmuir–Blodgett film properties of compounds 1–4

Compound			Area per molecule (nm^2)		Decay rate (cm^{2}min^{-1})		Transfer ratio (%)	
			pH 4	pH 9	pH 4	pH 9	pH 4	pH 9
1	a	$C_{14} \equiv H_{29}ThCH_2CO_2H$	26.4	26.6	0.13	0.39	109	–
	b	$C_{16} \equiv H_{33}ThCH_2CO_2H$	26.2	27.6	0.06	0.097	95	104
	c	$C_{17} \equiv H_{35}ThCH_2CO_2H$	25.6	29.5	0.073	0.078	93	–
	d	$C_{18} \equiv H_{37}ThCH_2CO_2H$	27.4	27.7	0.029	0.07	94	–
2	a	$C_{14} \equiv H_{29}ThCO(CH_2)_2CO_2H$	29.1	30.8	4.56	1.55	–	110
	b	$C_{16} \equiv H_{33}ThCO(CH_2)_2CO_2H$	31.6	31.5	0.42	0.39	–	103
	c	$C_{17} \equiv H_{35}ThCO(CH_2)_2CO_2H$	31.5	31.1	0.055	0.059	–	96
	d	$C_{18} \equiv H_{37}ThCO(CH_2)_2CO_2H$	31.6	31.1	0.042	0.074	95	–
3	a	$C_{14} \equiv H_{29}Th(CH_2)_3CO_2H$	25.3	26.3	–	0.057	93	99
	b	$C_{16} \equiv H_{33}Th(CH_2)_3CO_2H$	23.9	28.4	0.019	0.12	96	–
	c	$C_{17} \equiv H_{35}Th(CH_2)_3CO_2H$	24.9	28.5	0.019	0.028	97	–
	d	$C_{18} \equiv H_{37}Th(CH_2)_3CO_2H$	24.9	27.2	0.013	0.018	99	–
4		$C_9 \equiv H_{19}COTh(CH_2)_5CO_2H$	27.5	–	2.83	–	–	–

TABLE II Langmuir–Blodgett film properties of compound 5

Compound	Area per molecule (nm^2)			Decay rate (cm^2 min^{-1})			Transfer ratio (%)		
	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
Pure 5	19.5	22.0	24.0	1.15	0.32	0.17	48	54	71
30:70[a]		19.8			–			77	
50:50[a]		23.2			–			75	
67:33[a]		23.6			–			76	
Alt 3[b]		39.5			0.13			103[c]	
Alt 5[b]		35.5			0.09			98[c]	
Alt 7[b]		39.5			0.16			97[c]	
Alt 9[b]		38.6			0.15			103[c]	

Compound 5 1-(*N*-docosyl-5’-acetamido-2’-thienyl)-2-(4”-nitrophenyl)-ethene.

[a] Ratio of compound 5e to arachidic acid in the mixture. Experiments carried out at pH 9.0 and between 18 and 20°C.

[b] These are alternate layers of arachidic acid and the 67:33 mixture deposited on three layers of arachidic acid on glass. Experiments carried out at pH8.0 and between 18 and 20°C.

[c] These are average transfer ratios.

The transfer ratio of the monolayers is almost the same for all the compounds in groups one to four.

The results for compound 5 are shown in Table II. It can be seen in the pure compound 5 that the higher the pH of the subphase the higher the area per molecule and the more stable the monolayer is on the subphase. This leads to a better transfer ratio from the subphase to the substrate. The improved film stability under these conditions may be attributed to a greater tendency towards the formation of a dimer structure consisting of a large cadmium ion and two molecules of compound 5 associated through the–NO_2^- “head” group in a similar way to the carboxylic acid group in cadmium stearate.

The mixtures of compound 5 and arachidic acid were prepared in order to convey additional stability to the monolayers of compound 5. The transfer ratios of the various mixtures with different proportions of arachidic acid and compound 5 were all approximately the same. The 67:33 of compound 5 to arachidic acid was therefore chosen for subsequent experiments on alternate layer structures because it contained the highest concentration of active material. Alternating layer deposition had to be performed at pH 8, because films of arachidic acid are unstable at higher values of subphase pH. The superior transfer ratio of the mixtures when forming the alternating structures rather than monolayer films may be attributed to the arachidic acid component being more stable at the slightly lower pH employed in this set of studies.

4. Conclusion

A range of novel materials incorporating a thiophene moiety have been synthesized and screened for deposition by the Langmuir–Blodgett technique. The characterization of a D–π–A material has been extended to include a successful demonstration of the production of heterogeneous monolayer and alternate layer structures of the type which may exhibit second-order optical non-linearities.

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References

1. G.G. ROBERTS, *Contemp. Phys.* **2** (1984) 109.
2. D.J. WILLIAMS, *Angew. Chem. Int. Ed. Engl.* **23** (1984) 690.
3. G.J. ASHWELL, R.C. HARGREAVES, C.E. BALDWIN, G.S. BAHRA and C.R. BROWN, *Nature* **357** (1992) 393.
4. I.R. GIRLING, N.A. CADE, P.V. KOLINSKY, R.J. JONES, I.R. PETERSON, M.M. AHMAD, D.B. NEAL, M.C. PETTY, G.G. ROBERTS and W.J. FEAST, *J. Opt. Soc. Am. B* **4** (1987) 950.
5. G.J. ASHWELL, P.D. JACKSON, D. LOCHUN, P.A. THOMPSON, W.A. CROSSLAND, G.S. BAHRA, C.R. BROWN and C. JASPER, *Proc. R. Soc. Lond. Ser. A Math. Phys. Sci.* **445** (1994) 385.
6. HUANG-MINLON, *J. Am. Chem. Soc.* **68** (1946) 2487.
7. *idem, Ibid.* **71** (1949) 3301.
8. I. GOLDFARB. *J. Russ. Phys. Soc.* **62** (1930) 1073 (through *Chem. Abs.* **25**, 2719).
9. O.C. DERMER, D.M. WILSON, F.M. JOHNSON and V.H. DERMER, *J. Am. Chem. Soc.* **63** (1941) 2881.
10. A.V. GROSSE and V.N. IPATIEFF, *J. Org. Chem.* **1** (1936) 559.
11. H.D. HARTOUGH, “Thiophene and its derivatives” (Interscience, 1952).
12. A. KOZIARA, S. ZAWADZKI and A. ZWEIRZAK, *Synth. Commun.* July (1979) 527.
13. O. METH-COHN and B. NARINE, *Ibid.* February (1980) 133.
14. “Vogel’s Textbook of Practical Chemistry”, 4th Ed. (Longman 1978).

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