

Synthesis and Langmuir–Blodgett Films of a Zwitterionic D- π -A Adduct of Tetracyanoquinodimethane (TCNQ)

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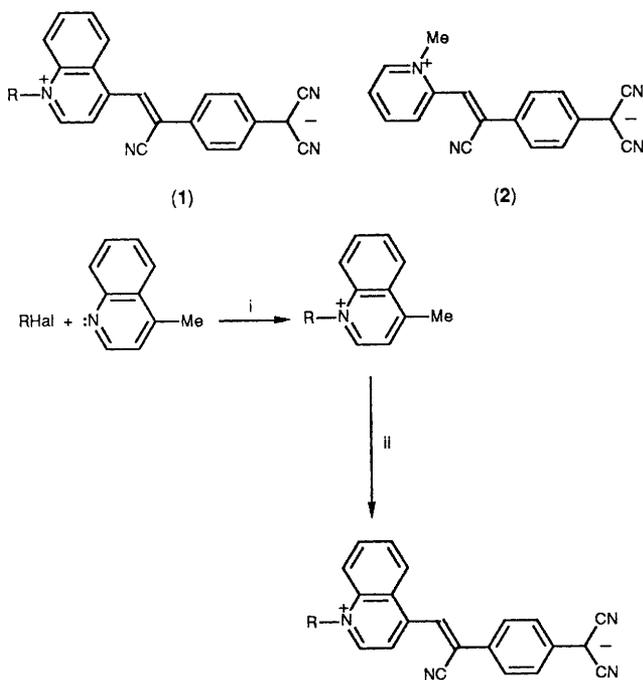
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The efficient synthesis of a range of highly polar novel zwitterionic D- π -A adducts of tetracyanoquinodimethane (TCNQ) has been established and derivatives with an alkyl chain as short as eight carbon atoms have been fabricated as Langmuir–Blodgett (LB) films.

The Langmuir–Blodgett (LB) technique¹ has been the subject of growing interest in recent years due to its ability to fabricate molecular arrays of a precise order and thickness. The application of these LB films in the field of molecular

electronics² is slowly being realised with films exhibiting, for example, electrical conduction,³ second harmonic generation,⁴ and molecular rectification.⁵ Here we report on novel zwitterionic D- π -A adducts (1) based on tetracyanoquinodimethane (TCNQ) whose highly polarised ‘push-pull’ nature suggests they may have non-linear optical properties.

The synthesis of the related compound (*Z*)- β -(1-methyl-2-pyridinium)- α -cyano-4-styryldicyanomethanide (2), and its full characterisation, was reported by one of us some time ago.⁶ The synthetic procedure used to prepare (2) was found to be time consuming and inefficient when applied to long chain, γ -substituted quinolinium analogues, *e.g.*, two weeks reflux when applied to a C₈ alkyl analogue. Compound (1) was



Scheme 1. Reagents and conditions: i, heat; ii, TCNQ, piperidine, MeCN, heat.

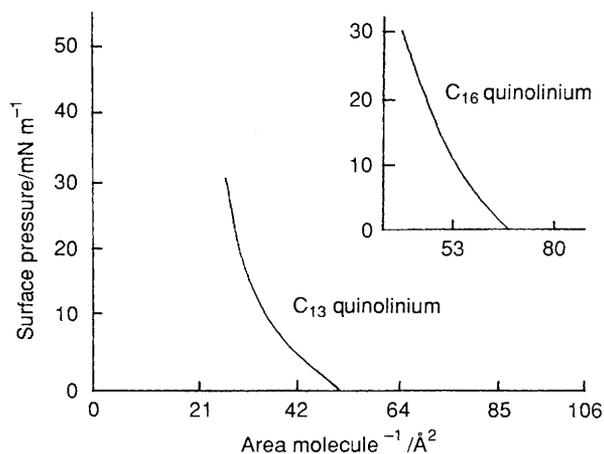


Figure 1

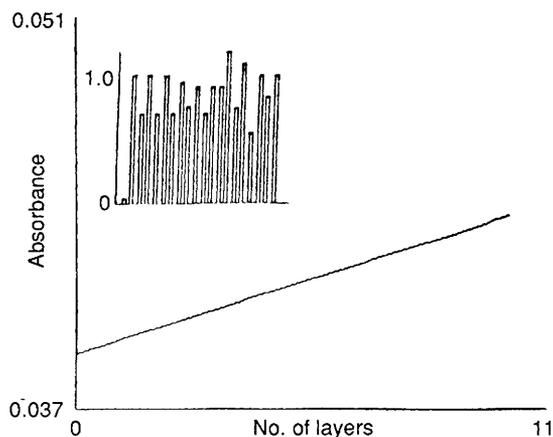


Figure 2

prepared from the condensation of equimolar quantities of the appropriate quinolinium donor and TCNQ in acetonitrile in the presence of piperidine (Scheme 1). The isolated product was washed with toluene and ether and recrystallised from hot acetonitrile. (Using this procedure, for example, the reaction time was cut to 8 h.) Microanalysis and comparison of spectroscopic data with (2) confirm the structure as that of (1) [ν ($C\equiv N$) 2200, 2150 cm^{-1} ; λ_{max} (MeCN) 709 nm]. As expected, the charge-transfer band at ca. 700 nm is solvatochromic, exhibiting a red shift with decreasing solvent polarity, consistent with a transition from an ionic to a neutral ground state.⁷ The ionic nature of the TCNQ moiety is shown by the two distinct $C\equiv N$ stretching vibrations at ν 2200 and 2150 cm^{-1} .

It was thought that using quinolinium rather than picolinium donors, where we have an extra fused aromatic ring, would enable shorter chain analogues to be fabricated as LB films.⁸ Derivatives of (2), where R^1 is an alkyl chain longer than seven carbon atoms, are insoluble in many organic solvents, but can be spread from dichloromethane solution ('Aristar' grade) onto a pure water subphase (18 M Ω Milli-Q). Using a Joyce-Loebl Langmuir Trough 4, the compounds were found to form monomolecular layers at the air-water interface (Figure 1) with collapse pressures in excess of 50 mN m^{-1} (subphase temp. 21 $^\circ$, compression rate 1.0 $\text{cm}^2 \text{min}^{-1}$, pH 5.6). The effect of changing pH and the addition of divalent metal ions (e.g., Cd^{2+}) was minimal. Negligible hysteresis was observed on film expansion. The resulting compressed monolayers are very stable, a 0.1% area decrease in 1 h being typical. The observed molecular areas are quite small, being in the range 25–50 \AA^2 per molecule and we conclude that the chromophore is orientated perpendicular to the water surface with the aliphatic chains pointing away from the water.

Transference of monolayers of (2) onto a variety of hydrophilic substrates (e.g., quartz slides) occurs readily. The compacted monolayers were transferred at a surface pressure of 25 mN m^{-1} by slowly dipping and raising the substrate through the compacted film. Figure 2 shows that predominantly 'Y' type deposition occurs with a transfer ratio of unity on both the 'up' and 'down' strokes. The reproducibility of each monolayer is confirmed by the linear plot of absorbance vs. number of layers. Interestingly, there appears to be a change in the UV-VIS absorbance spectra of the films with increasing alkyl chain length (Figure 3). It is thought that this is due to a change in the molecular alignment of the

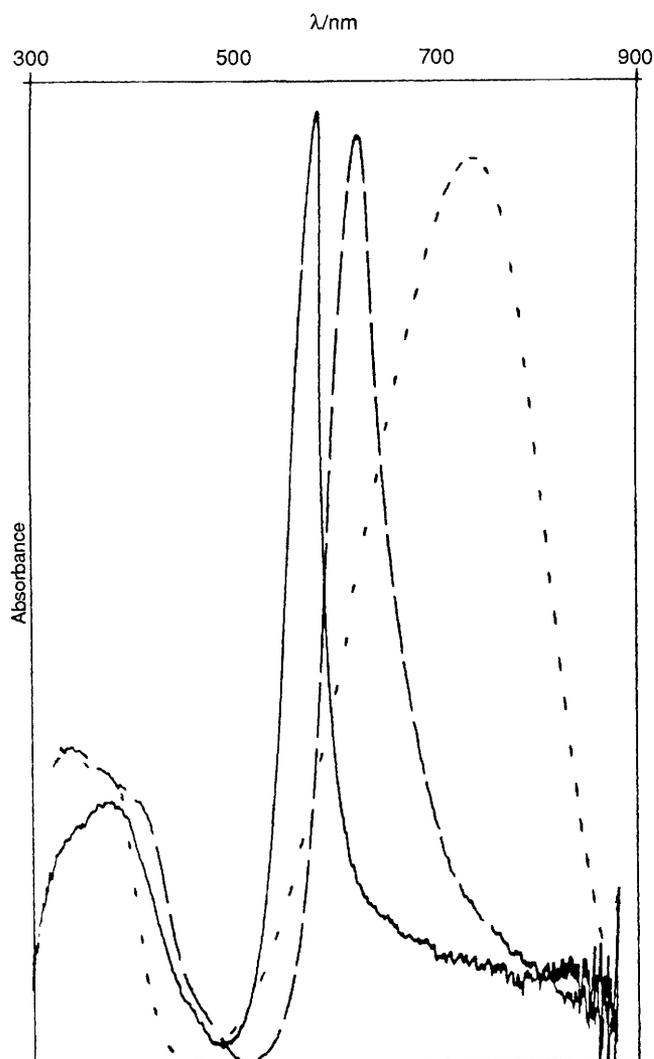


Figure 3. UV-VIS absorbance spectra of the zwitterions. (—) C_{20} quinolinium (LB film); (— — —) C_{11} quinolinium (LB film); (- - - -) C_8 quinolinium (MeCN solution).

chromophore resulting in a change from an intermolecular to an intramolecular transition.

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