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Liquid Crystals

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2,3,7,8,12,13-Hexakis[2-(2-methoxyethoxy)ethoxy]-tricycloquinazoline: a discogen which allows enhanced levels of n-doping

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A synthesis has been developed for 2,3,7,8,12,13-hexakis[2-(2-methoxyethoxy)ethoxy]-tricycloquinazoline (TCQ6EO2M) in which the ethylenoxy side chains are introduced before elaboration of the heterocylic core. This discogen gives a hexagonal columnar phase (Col_h) between 77 and 233°C. n-Doping using potassium metal is facilitated firstly by the electron poor/π-deficient nature of the core and secondly by the polyethylenoxy side chains which complex the potassium K^+ counter-ions. The conductivity of the Col_h phase of TCQ6EO2M doped with 10 mol% potassium ($\sigma_{\parallel} = 1.1 \times 10^{-3}$ S m^{-1}) is substantially higher than that previously reported for 2,3,7,8,12,13-hexa(hexylthio)tricycloquinazoline doped with 6 mol% potassium ($\sigma_{\parallel} = 2.9 \times 10^{-5}$ S m^{-1}). Photoconductivity studies of TCQ6EO2M using a time of flight sample configuration show transient photocurrents for both holes and electrons. From these an upper limit on the mobility for the electrons is estimated as $\sim 10^{-4}$ cm^2 V^{-1} s^{-1} at 150°C which is of the same magnitude as that for hole mobilities in other columnar discotic liquid crystals.

1. Introduction

Conducting discotic liquid crystals [1] combine the electrical properties of semiconductors with the anisotropic properties of (LCs) affording prospects of significant applications [2]. Since, in common with most organic crystalline solids, pure discotic LCs are intrinsically insulating, charge carriers have to be injected. The original and perhaps simplest method for doing this is chemical 'doping'. In most of the cases studied to date this has involved 'p-doping' in which an electron is removed from the core of a π-excessive discogen using an oxidizing agent [1]. For example, when 2,3,6,7,10,11-hexahexyloxytriphenylene (HAT6) **1** is doped with 1 mol% of the electron acceptor aluminium chloride, the conductivity σ increases from an undoped value of less than 10^{-9} S m^{-1} to about 10^{-3} S m^{-1}, with the conductivity along the columns ($\sigma_{\parallel}$) being about three orders of magnitude greater than that in the perpendicular direction ($\sigma_{\perp}$) [3].

In principle, conducting discotic LCs can also be made by treating a discogen with a π-deficient aromatic core with a reducing agent (n-doping). Compared with p-doped discotic LCs, few examples of n-doped discotic LCs are known. However, we have shown that the electron-deficient system 2,3,7,8,12,13-hexakis(hexylthio)-tricycloquinazoline **2** can be doped with alkali metals [4]. For example, doping of compound **2** with 6 mol% of potassium gives a system in which the conductivity in the columnar phase parallel to the columns ($\sigma_{\parallel}$) is 2.9×10^{-5} S m^{-1} and the anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) is 518. We argued that the conductivity and level of doping in **2** were limited by the low solubility of the potassium K^+ counter-ions in the hydrocarbon side chain matrix and that replacing the hexylthio side chains of compound **2** with ethylenoxy chains, as in TCQ6EO2M **3**, should enhance the K^+ solubility leading to higher doping levels and higher conductivities. This proves to be the case. Flash photolysis provides an alternative method for injecting charge carriers into discotic LC systems. For most discotic LCs time-of flight photoconductivity studies have been limited to hole transport studies. Electron transients are generally very small and difficult

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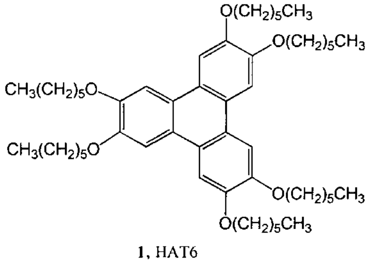
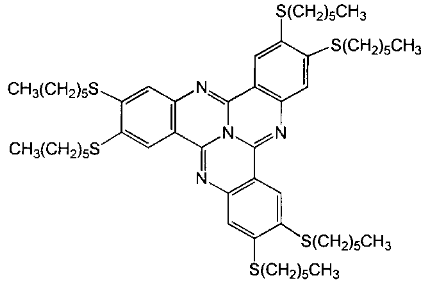
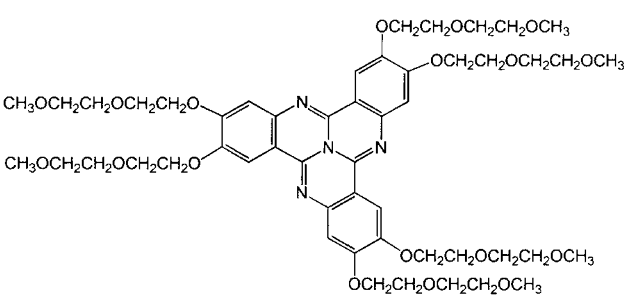
to observe, reflecting the limited range of electrons in these materials. However, for TCQ6EO2M **3**, both hole and electron transient photocurrents can be obtained. This also reflects the electron-deficient nature of the tricycloquinazoline core.



1, HAT6



2



3, TCQ6EO2M

2. Synthesis

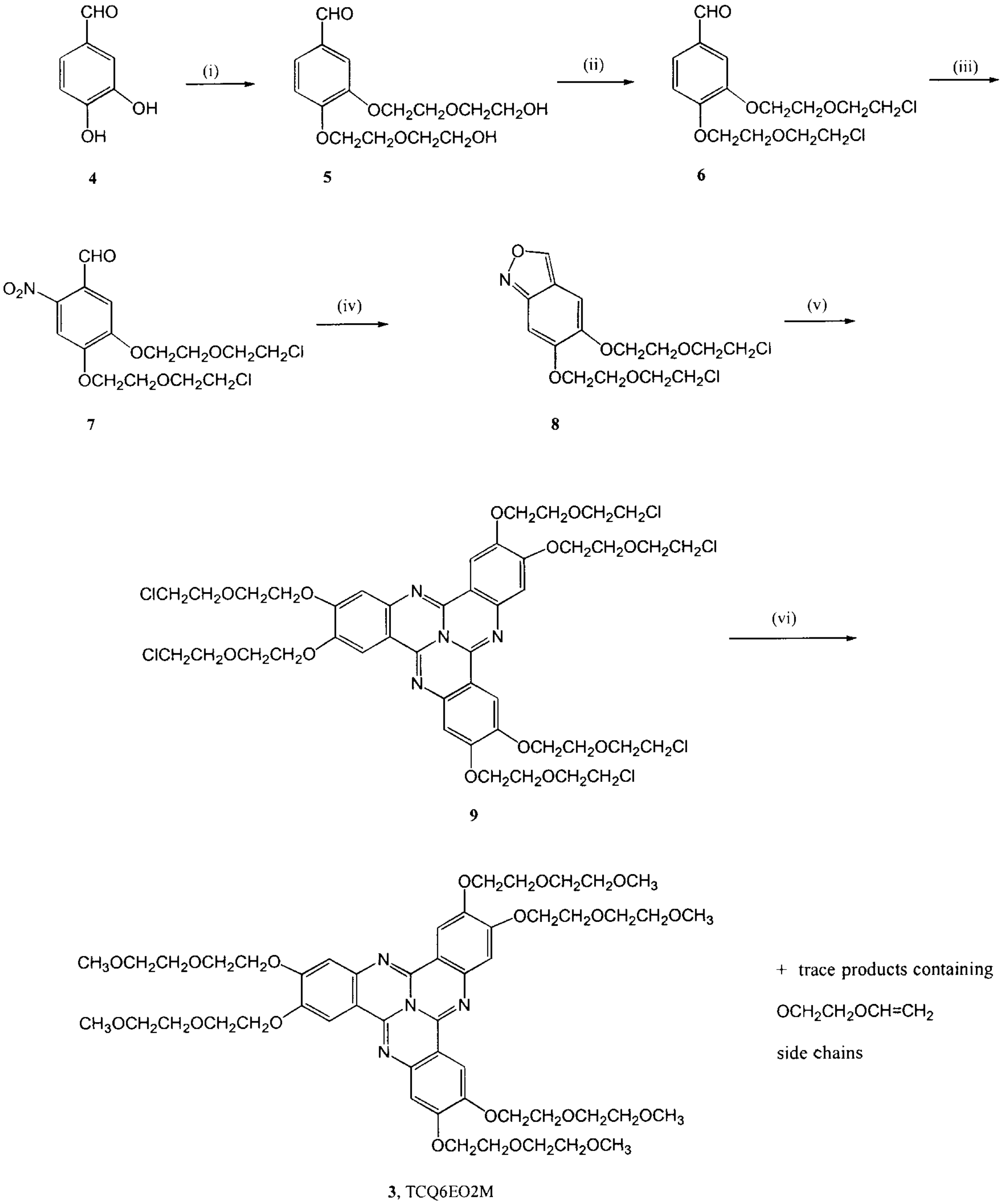
The tricycloquinazoline core is thermally and chemically stable [5]. It has been widely studied by both chemists and biologists mainly because of interest in the carcinogenic activity of the parent heterocycle and of some of its simple derivatives [6]. Derivatives bearing six alkoxy or alkthio side chains have been synthesized and shown to be mesogenic [5, 7]. In the synthesis of tricycloquinazolines, the main problem is that of assembling the hetrocyclic core in high yield. In the case of compound **3**, the synthesis is further complicated by the presence of the ethylenoxy side chains which makes the purification of the product and intermediates by column chromatography more difficult. Initially we used 2,3,7,8,12,13-hexahydroxytricycloquinazoline in reaction with 1-bromo-2-(2-methoxyethoxy)ethane/potassium hydroxide [5], but the desired product **3** was obtained in very poor yield. Hence routes were explored in which the side chains were introduced before formation of the tricycloquinazoline core. What at first appeared an excellent solution to the problem involved the synthesis of compound **8** which was trimerized to give compound **9** [5] (scheme 1). These products with chloro-terminated side chains were much easier to purify by chromatography than analogues with methoxy terminated chains. Compound **3** could be made by treating compound **9** with methoxide but, when prepared by this route, it always gave transition temperatures a few degrees below that of the absolutely pure product. Eventually the problem was traced to minor vinyl ether-containing by-products produced by elimination of hydrogen chloride in the reaction with methoxide. These were detected by both ^{1}H NMR spectroscopy (δ_H 6.6, 4.3, and 4.1) and MS ($M^+ - 32$, $M^+ - 64$). They proved inseparable from compound **3** by chemical methods, column chromatography or recrystallization. Attempts to replace the chlorine of compound **8** with methoxide were unsuccessful because of the base-sensitivity of the heterocyclic ring. It is clear that the ethylenoxy side chains had to be introduced by another method.

The most successful synthetic route of many which we have explored [8] is shown in scheme 2. 6-Nitropiperonal **10** was converted into 4,5-dihydroxy-2-nitrobenzaldehyde **11** in 85% yield [9]. Acylation of **11** with acetic anhydride/sodium acetate gave compound **12** in excellent yield [9] and further reaction with 1-bromo-2-(2-methoxyethoxy)-ethane/potassium carbonate in dimethylsulphoxide gave compound **13**. Compound **13** was reduced to 5,6-bis-[2-(2-methoxyethoxy)ethoxy]anthranil **14** in 44% yield [5, 7]. Trimerization of compound **14** is still the weak step in the sequence, giving at best an 18% yield. Refluxing in ammonium acetate/glacial acetic acid for 67 hours gave the desired product **3** which was purified by silica gel column chromatography and recrystallizations from diethyl ether/dichloromethane.

3. Liquid crystal behaviour of TCQ6EO2M

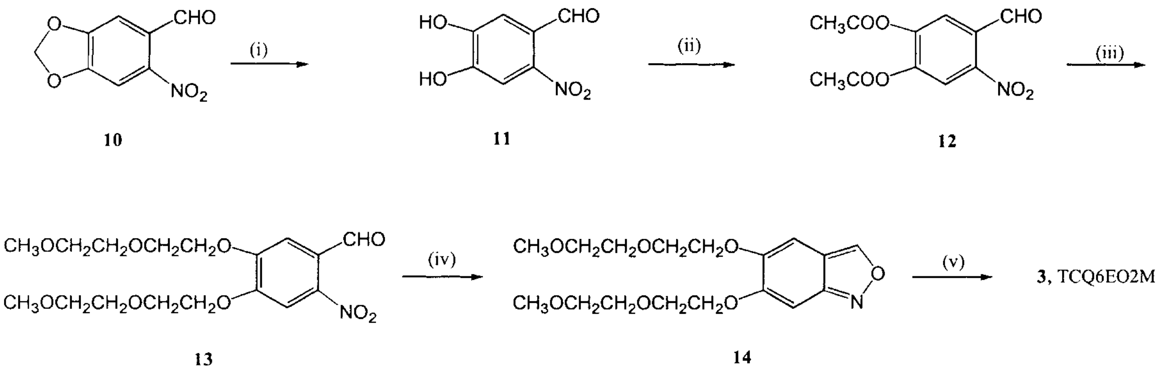
Compound **3** has a broad mesophase range from 77 to 233°C. DSC showed that the melting and clearing transitions are reproducible in both heating and cooling cycles. Optical microscopy suggests that compound **3** gives a hexagonal columnar mesophase (Col_h). Samples cooled from the isotropic phase give a dendritic texture with large homeotropic domains. Figure 1 shows a typical photomicrograph obtained after slowly cooling the isotropic phase to 230°C.

Low angle X-ray diffraction (XRD) studies of compound **3** at 230°C show a single reflection corresponding to a *d*-spacing of 19 Å. If one assumes a hexagonal lattice, this can be assigned to the 1 0 0 (*h k l*) reflection.



Scheme 1. Synthesis of TCQ6EO2M via the corresponding ω-chloro compound. Reagents: (i) $HOCH_2CH_2OCH_2CH_2Cl/K_2CO_3$/EtOH, 52%; (ii) $SOCl_2/CH_2Cl_2$, 35%; (iii) conc. HNO_3/HOAc, 71%; (iv) Sn/HOAc, 41%; (v) NH_4OAc/AcOH, 15%; (vi) MeONa/MeOH/DMSO.

Hexakis(pentylthio)tricycloquinazoline [7], which has a side chain length approximately equal to that of TCQ6EO2M, has a 1 0 0 reflection at 18.4 Å together with a very weak 1 1 0 reflection at 10.8 Å. This 1 1 0 reflection is not seen for TCQ6EO2M. This could mean that the system is relatively disordered, perhaps as a result of the higher incidence of *gauche*-conformations associated with ethylenoxy side chains [10]. Preliminary studies have shown that TCQ6EO2M [8] forms at least two lyotropic mesophases (Col_h and N_{col}) in water [11, 12]. Studies aimed at mapping the phase diagram of the TCQ6EO2M/water system and at understanding the aggregation behaviour of TCQ6EO2M in dilute solution are in progress.



Scheme 2. Improved synthesis of TCQ6EO2M. Reagents: (i) $AlCl_3/CH_2Cl_2$, HBr (48%) 89%; (ii) Ac_2O/AcONa, 96%; (iii) $BrCH_2CH_2OCH_2CH_2OCH_3$/KOH/DMSO, 80%; (iv) Sn/HOAc, 57%; (v) NH_4OAc/AcOH, 18%.

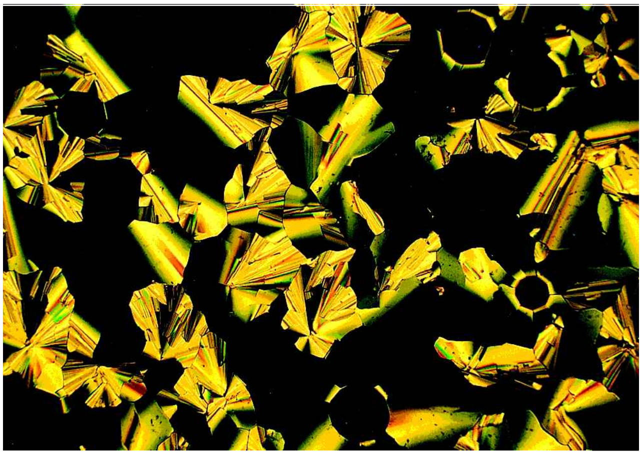


Figure 1. Optical texture seen using polarizing optical microscopy for TCQ6EO2M at 230°C illustrating a typical Col_h phase texture (magnification ×150).

4. Electrical conductivity of TCQ6EO2M

Levels of n-doping of compound **2** with potassium are limited to a maximum of *ca.* 6 mol % by the low solubility of the potassium cations in the hydrocarbon side chain matrix [4]. We reasoned that by replacing the hexylthio side chains of compound **2** with ethylenoxy chains, as in compound **3**, the solubility of potassium cations would be enhanced and higher doping levels and higher conductivities would be achieved. We found that TCQ6EO2M **3** can be doped with at least 10 mol % of potassium (we have not yet explored the upper doping limit). The d.c. conductivity studies were made on aligned samples of undoped and potassium doped TCQ6EO2M; the results are summarized in table 1.

Table 1. Comparison of the conductivity σ of undoped TCQ6EO2M with that of potassium-doped (10 mol %) TCQ6EO2M in the crystalline phase (29°C), columnar Col_h phase (160°C) and isotropic phase (250°C).

	Conductivity σ/S m^{-1}	
Temperature/°C	Undoped TCQ6EO2M	K-doped TCQ6EO2M (10 mol %)
29	5.714×10^{-9}	8.85×10^{-4}
160	6.073×10^{-8}	1.058×10^{-3}
250	6.69×10^{-7}	1.071×10^{-3}

As can be seen from table 1, the conductivity increases by *c.* 2×10^{-4} S m^{-1} on going from the crystalline phase to the Col_h phase. Of much greater interest is the five orders of magnitude rise in conductivity when TCQ6EO2M is doped with potassium. The conductivity of TCQ6EO2M doped with 10 mol % potassium ($\sigma_\parallel = 1.1 \times 10^{-3}$ S m^{-1}) is much higher than that of hexa(hexylthio)tricycloquinazoline **2** doped with 6 mol % potassium ($\sigma_\parallel = 2.9 \times 10^{-5}$ S m^{-1} in the Col_h phase) and is comparable to that of HAT6 doped with 5 mol % aluminium chloride $AlCl_3$ (p-doped, $\sigma_\parallel = 5 \times 10^{-2}$ S m^{-1} in the Col_h phase), in agreement with earlier studies which suggest a very similar charge-carrier mobility.

5. Transient photoconductivity studies

For most discotic liquid crystals, time of flight photoconductivity studies have been limited to hole transport studies. However, for compound **3**, which has a relatively electron-poor core, both hole and electron transport were observed and are shown in figure 2. Since transient photocurrents rather than transits were obtained, we can conclude that the carrier range S is less than the sample thickness d (6 μ in most cases). Under these circumstances limited information (only) can be obtained from the integrated photocurrent $\int i\mathrm{d}t$ and peak photocurrent i_p. We can write:

$$\int_0^\infty i\mathrm{d}t = eN_\mathrm{Ph}\{\eta\phi\}(S/d)$$

$$i_\mathrm{p} = eN_\mathrm{Ph}\{\eta\phi\}(v_\mathrm{D}/d)$$

where N_Ph is the number of photons absorbed, e is the charge on the electron and v_D is the carrier drift velocity. The quantum efficiency, $\{\eta\phi\}$, is written as the product

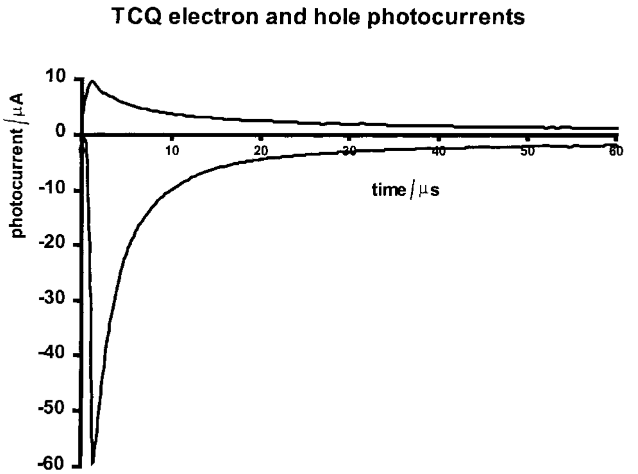


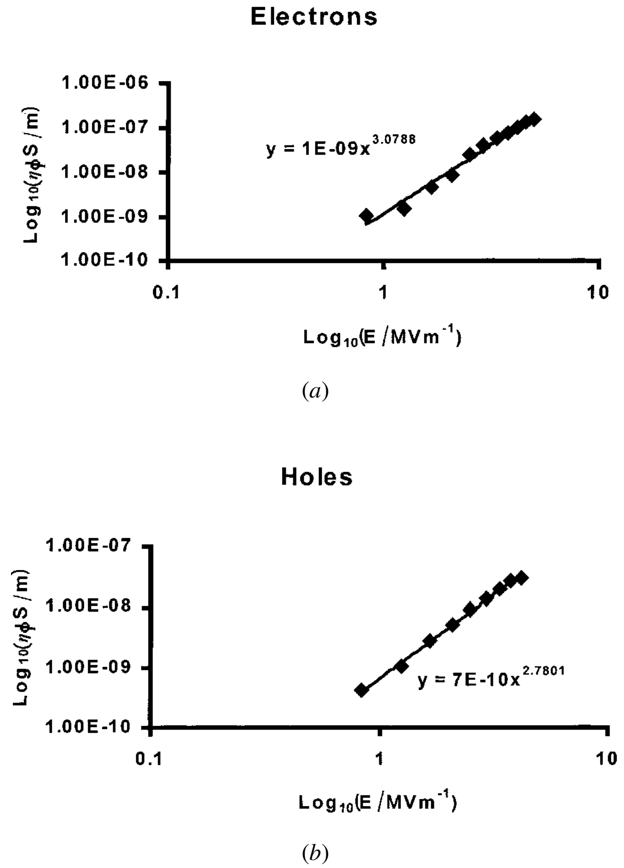
Figure 2. Typical photocurrents for compound **3** for electron (negative) and hole charge-carriers; Al/TCQ6EO2M/Al at 150°C measured at 2.5 mV m^{-1}.

of two quantities: η represents the primary quantum efficiency for carrier pair creation and ϕ is the probability that the pair avoid geminate recombination. Since e, N_{Ph} and d are known, we are able to measure the products $\{\eta\phi\}S$ and $\{\eta\phi\}v_{\mathrm{D}}$ and determine how these quantities vary with electric field.

Figures 3(*a*) and 3(*b*) show the electric field dependence of $\{\eta\phi\}S$ for electrons and holes, respectively, on a double log plot. Over the limited range of electric field available, the data have been fitted to a power law. Figures 4(*a*) and 4(*b*) show the electric field dependence of $\{\eta\phi\}v_{\mathrm{D}}$ for electrons and holes, respectively, again on a double log plot. Once again a simple power law may be used to describe the behaviour over the limited electric field range. Since v_{D} varies linearly with field, as demonstrated for discotic materials where time of flight transits are available [13], we may deduce from the field dependence of $\{\eta\phi\}v_{\mathrm{D}}$ the field dependence of $\{\eta\phi\}$.

Most interestingly, the power laws thus found for the generation efficiency $\{\eta\phi\}$ for electrons and holes are very different. This would not be the case if the production mechanism produced both signs of carriers pairwise. The implication must be that there are two photogeneration mechanisms for the electrons. A possibility is that there is pair-wise electron–hole generation across an energy gap varying as $\mathbf{E}^{0.5}$, as reflected in the field dependence of $\{\eta\phi\}$ for holes, together with electron photoinjection from the aluminium electrode that is linear in field. The linearity may be ascribed to geminate recombination of the photoinjected electron with its image charge in the electrode.

The behaviour of photoinjected carriers into organics has been given a theoretical treatment using a modified version of the Onsager theory of ion dissociation. The recombination of injected carriers with their image charge can be treated as a one-dimensional version of the Onsager problem. Such treatment by Blossey [14] has led to a linearity in escape probability with electric field as suggested here. A further interesting matter is the actual value (for electrons at highest field) of $\{\eta\phi\}S = 1.5 \times 10^{-7}$ m. Since $S < 6\,\mu$ there is a lower limit to be placed on the quantum efficiency for carrier creation,



(*a*)

(*b*)

Figure 3. Double logarithmic plots of field versus the product $\eta\phi S$ for (*a*) electron and (*b*) hole charge-carriers in Al/TCQ6EO2M/Al at 150°C.

$$\{\eta\phi\} > 2.5 \times 10^{-2}.$$

This is a surprisingly high value. Similar reasoning, using the lower limit of $\{\eta\phi\}$ places an upper limit on the mobility of the electrons,

$$\mu_{\mathrm{e}} < 4.5 \times 10^{-4}\ \mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}.$$

This is close to the hole mobility value for HAT6. The measured and deduced power law dependences of the quantities, $\{\theta\phi\}S$, $\{\eta\phi\}v_{\mathrm{D}}$, $\{\eta\phi\}$ and S are grouped together in table 2. The deduced field dependence of the carrier range, S, is currently without explanation. In three-dimensional materials, S would vary linearly with electric field, whereas in one dimension S would be a material constant independent of field.

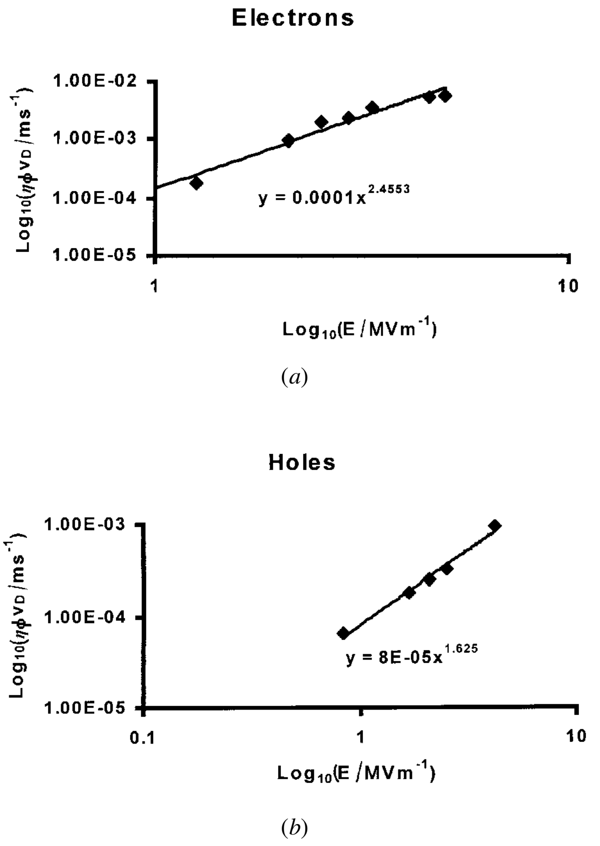


Figure 4. Double logarithmic plots of field versus the product $\eta\phi v_D$ for (*a*) electron and (*b*) hole charge-carriers in Al/TCQ6EO2M/Al at 150°C.

Table 2. Photoconductivity of TCQ6EO2M at 150°C. Over a limited electric field **E**, power laws were fitted to describe the electric field dependence of the quantum efficiency for carrier production and of the carrier range for electrons and holes. The quantum efficiency dependence has been deduced from figure 4 with the assumption that the velocity of the carrier is linear in field-with the deduction of the field dependence of the quantum efficiencies, the field dependence of the carrier range follows from figure 3.

Parameter	Holes	Electrons	Origin
$\eta\phi S$	$\mathbf{E}^{2.8}$	$\mathbf{E}^{3.1}$	Measured (Integrated photocurrent)
$\eta\phi v_D$	$\mathbf{E}^{1.6}$	$\mathbf{E}^{2.5}$	Measured (Peak photocurrent)
$\eta\phi$	$\mathbf{E}^{0.6}$	$\mathbf{E}^{1.5}$	Assuming $v_D \propto \mathbf{E}^{1.0}$
S	$\mathbf{E}^{2.2}$	$\mathbf{E}^{1.6}$	Deduced

6. Conclusions

These studies serve to illustrate the way in which the properties of conducting discotic liquid crystals can be engineered at the molecular level. TCQ6EO2M **3** was designed with a relatively electron poor/π-deficient core and polyethylenoxy side chains to complex group 1 metal counter-ions. Together these facilitate the hoped-for high levels of n-doping with potassium metal. The electron poor/π-deficient nature of the core probably also contributes to the (unusual) observation of electron transient photocurrents. The mobility obtained for electron charge-carriers is similar to that previously reported for hole charge-carriers in related systems.

7. Experimental

7.1. *Instrumentation and general procedures*

DSC was carried out on Perkin-Elmer DSC2 and DSC7 machines. All polarizing optical microscopy measurements were made on a Vickers M17 polarizing microscope equipped with a Mettler POM FP 82HT hot stage and a Mettler FP90 control unit. The samples for low angle XRD were prepared in 0.7 mm capillary tubes which were then sealed. A pin-hole camera operating with Ni-filtered CuK$_\alpha$ radiation at 1.54 Å was used. Exposure times varied from 3 to 12 h depending on the intensity of the reflections. Melting points were determined using a Reichert Hot Stage. The proton spectra were recorded on a General Electric QE300 spectrometer, operating at 300 MHz. Mass spectrometry was done on a VG Autospec instrument. Ultraviolet and visible range spectra were recorded with the solvent staged using a Pye-Unicam PU8800 UV/Vis spectrophotometer and 1 cm cells. Infra-red spectra were recorded using a Philips PU9706 spectrophotometer and NaCl discs. Microanalysis was carried out by the staff of the School of Chemistry, University of Leeds. TLC was performed on precoated Riedel-deHaen 60F 254 aluminium backed sheets (Aldrich Chemical Co.). Plates were examined under UV light (254 nm) or by exposure to iodine vapour. Column chromatography on silica gel refers to the use of Merck Kieselgel 7731 type 60. Solvents were purified, when needed, according to the procedures described in [15].

7.2. *Procedure for making a TCQ6EO2M/K-doped sample*

The doped sample was prepared by adding a small length of potassium wire to 250 mg TCQ6EO2M in a small vessel which was quickly joined to a high vacuum line; the vessel was then sealed under the vacuum. In order to make a 10 mol % TCQ6EO2M/K sample, 1 mg of potassium was needed. Two techniques were used to obtain this as this was too small an amount to weigh out accurately (especially as potassium very quickly acquires an oxide coating when exposed to air). Small chunks of potassium were passed through a 0.6 mm bore sodium press into petroleum ether; measured lengths of this wire were weighed out in order to establish the length of wire that was equivalent to 1 mg. Alternatively, the volume of wire needed for 1 mg of potassium was calculated from $D = M/V$, where D = density, M = mass, and $V=$ volume $(=\pi r^2 l)$ where r is the radius of the wire (bore) and l is the required length. Both these estimates arrived at roughly the same length, which was 4 mm. The sample was then homogenized by heating, first with a hot gun at 100°C to melt the potassium, and then at 260°C in a Wood's metal bath, rotating frequently. The vessel was then transferred to a glove box where it was opened and the doped mesogen transferred to the measurement cell.

7.3. *Electrical conductivity measurements on TCQ6EO2M and on a K-doped TCQ6EO2M sample*

The conductivity of thin layers of both TCQ6EO2M and of a TCQ6EO2M/K-doped sample were measured using a two probe method and a Keithley 617 digital electrometer in picoammeter mode. Temperature was controlled to within ± 0.5 K using an Oxford Instruments DT22 controller.

7.4. *Time of flight conductivity measurements on TCQ6EO2M*

Homeotropic samples of TCQ6EO2M between aluminium electrodes were subjected to a 6 ns pulse from a Lambda Physic EMG101 nitrogen laser at 337 nm. The light intensity was modulated using neutral density filters and the resulting photocurrents monitored as previously described [16].

7.5. *Synthesis procedures*

7.5.1. *3,4-Bis[2-(2-hydroxyethoxy)ethoxy]-benzaldehyde (**5**)*

3,4-Dihydroxybenzaldehyde (**4**) (50 g, 0.37 mol), 2-(2-chloroethoxy)ethanol (97 ml, 0.93 mol) and potassium carbonate (130 g, 1.3 mol) were heated under reflux in ethanol (500 ml) under nitrogen for 70 h and then allowed to cool. Dichloromethane was added, the reaction mixture was filtered, and the solvent in the filtrate removed on a rotary evaporator. The residue was treated with dilute HCl and then washed with ether (to remove unreacted side chain). The aqueous layer was shaken with dichloromethane and the extracts were washed with dilute aqueous KOH and with water. They were dried (Na_2SO_4) and the solvent removed *in vacuo* to leave a brown oil, 3,4-bis[2-(2-hydroxyethoxy)ethoxy]-benzaldehyde (**5**) (59 g, 52%). Found: M^+, 314.1346; $C_{15}H_{22}O_7$ requires M^+, 314.1365. ^1H NMR (D_6-acetone) δ 9.85 (s, 1H, Ar–CHO), 7.52 (m, 2H, protons in the 2- and 6-positions on the aromatic ring), 7.02 (s, 1H, proton in the 2-position on the aromatic ring), 4.27 (t, $J=7$ Hz, 4H, Ar–OCH_2), 4.0 (t, $J=7$ Hz, 4H, Ar–$OCH_2C\underline{H}_2$), 3.65 (m, $J=7$ Hz, 8H, Ar–$OCH_2CH_2OC\underline{H}_2C\underline{H}_2OH$), 3.03 (broad s, 1H, OH). EIMS: m/z (%) 314 (M^+, 7), 164(22), 149(16), 107(14), 93(63), 83(79), 63(75), 59(21), 45(100).

7.5.2. *3,4-Bis[2-(2-chloroethoxy)ethoxy]-benzaldehyde (**6**)*

Thionyl chloride (15.6 ml, 0.2 mol) in dichloromethane (50 ml) was added dropwise over about 2 h to a stirred mixture of compound **5** (27 g, 0.089 mol) and pyridine (17.6 ml, 0.2 mol) in dichloromethane (250 ml) under nitrogen. The mixture was left under reflux for 2 h, stirred overnight at room temperature, and then heated under reflux for another 4 h. It was then poured into water, the organic layer was separated, and the aqueous layer shaken with dichloromethane. The combined extracts were washed with water, dried ($MgSO_4$), and subjected to column chromatography on silica gel using petroleum ether/ethyl acetate (2/1) as eluant, increasing the concentration of ethyl acetate with time, to isolate 3,4-bis[2-(2-chloroethoxy)ethoxy]benzaldehyde (**6**) as a dark viscous oil (10.4 g, 35%). ^1H NMR ($CDCl_3$) δ 9.89 (s, 1H, Ar–CHO), 7.48 (m, 2H, protons in the 2- and 6-positions on the aromatic ring), 7.0 (s, 1H, proton in the 2-position on the aromatic ring), 4.21 (t, $J=7$ Hz, 4H, Ar–OCH_2), 3.95 (t, $J=7$ Hz, 4H, Ar–$OCH_2C\underline{H}_2$), 3.85 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OC\underline{H}_2$), 3.66 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OCH_2C\underline{H}_2Cl$).

7.5.3. *4,5-Bis[2-(2-chloroethoxy)ethoxy]-2-nitrobenzaldehyde (7)*

Concentrated nitric acid (~50 ml) was added dropwise to compound **6** (4 g, 0.0114 mol) in glacial acetic acid (80 ml) whilst stirring at room temperature. The reaction was left to stir for 21 h, when the mixture was poured into water and shaken with dichloromethane; the extracts were washed twice with potassium carbonate solution and then with water, dried (Na_2SO_4), and the solvent removed *in vacuo* to leave an orange/brown solid. This was precipitated from dichloromethane with petroleum ether to give a yellow solid, 2-nitro-4,5-bis-[2-(2-chloroethoxy)ethoxy]benzaldehyde (**7**), which was collected by vacuum filtration (3 g, 71%), m.p. 70°C. Found: M^+, 395.0541; $C_{15}H_{19}Cl_2NO_7$ requires M^+, 395.0539. ^1H NMR ($CDCl_3$) δ 10.5 (s, 1H, ArCHO), 7.7 (s, 1H, proton in the 3-position on the aromatic ring), 7.5 (s, 1H, proton in the 6-position on the aromatic ring), 4.2 (t, $J=7$ Hz, 4H, Ar–OCH_2), 3.95 (t, $J=7$ Hz, 4H, Ar–$OCH_2C\underline{H}_2$), 3.85 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OC\underline{H}_2$), 3.65 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OCH_2C\underline{H}_2Cl$). EIMS: m/z (%) 396 (M^+, 53), 289(14), 209(54), 179(33), 107(98), 63(100), 51(15), 45(100).

7.5.4. *5,6-Bis[2-(2-chloroethoxy)ethoxy]anthranil (**8**)*

Tin powder (3.6 g, 0.03 mol) and compound **7** (2.95 g, 7.5 mmol) were stirred in glacial acetic acid (50 ml) at room temperature for 6 h and then ether was added. The mixture was filtered, and filtrate washed with water, and the organic layer separated and washed twice with potassium carbonate solution and then with water. It was dried (Na_2SO_4) and the solvent removed *in vacuo* to leave a viscous red liquid which was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate (2/1) as eluant, increasing the concentration of ethyl acetate with time. The reduced compound, 5,6-bis[2-(2-chloroethoxy)ethoxy]anthranil (**8**), was isolated as a thick yellow oil which later solidified (1.1 g, 41%), m.p. 63–66°C. Found: M^+, 363.0638; $C_{15}H_{19}Cl_2NO_5$ requires 363.0640. ^{1}H NMR ($CDCl_3$) δ 8.85 (s, 1H, proton on the heterocyclic ring), 6.79 (s, 1H, proton in the 7-position), 6.72 (s, 1H, proton in the 4-position), 4.25 (t, $J=7$ Hz, 2H, Ar–OCH_2), 4.18 (t, $J=7$ Hz, 2H, Ar–OCH_2), 4.0 (t, $J=7$ Hz, 4H, Ar–$OCH_2C\underline{H}_2$), 3.92 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OC\underline{H}_2$), 3.65 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OCH_2C\underline{H}_2Cl$). EIMS: *m*/*z* (%) 363 (M^+, 100), 257(49), 232(37), 177(39), 160(36), 150(54), 124(12), 107(25), 63(30), 43(16), 32(55).

7.5.5. *2,3,7,8,12,13-Hexa[2-(2-chloroethoxy)ethoxy]-tricycloquinazoline (9)*

Compound **8** (350 mg, 0.92 mmol) and ammonium acetate (240 g, 2.76 mmol) were stirred in glacial acetic acid (8 ml) under argon, at 100–120°C for 49 h and then the reaction mixture was allowed to cool. It was poured into water and shaken with dichloromethane. The organic layer was separated, washed twice with potassium carbonate solution and then with water, dried (Na_2SO_4), and the solvent removed *in vacuo* to leave a dark brown solid. This was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate (1/1) as eluant, increasing the concentration of ethyl acetate with time. The trimer **9** was isolated, and precipitated from dichloromethane with petroleum ether as a green solid (54 mg, 15%), m.p. 120–122°C. ^{1}H NMR ($CDCl_3$) δ 7.5 (s, 3H, aromatic protons in the 4-, 9- and 14-positions), 6.72 (s, 3H, aromatic protons in the 1-, 6- and 11-positions), 4.25 (t, $J=7$ Hz, 2H, Ar–OCH_2), 4.18 (t, $J=7$ Hz, 2H, Ar–OCH_2), 4.0 (t, $J=7$ Hz, 4H, Ar–$OCH_2C\underline{H}_2$), 3.88 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OC\underline{H}_2$), 3.65 (t, $J=7$ Hz, 4H, $ArOCH_2CH_2OCH_2C\underline{H}_2Cl$). FABMS: *m*/*z* (%) 1056 (M^+, 100), 1018(16), 949(18), 869(9).

7.5.6. *Attempted preparation of TCQ6EO2M **3** via substitution of the chlorides on **9** with methoxide*

Compound **9** (50 mg, 0.05 mmol), was stirred in boiling methanol (5 ml) and DMSO (5 ml). Sodium methoxide (excess) was added and the mixture was left to stir at 70°C for 100 h under nitrogen; it was then allowed to cool. Water was added and the mixture was shaken with dichloromethane; the extracts were washed with dilute HCl, and the solvent was removed *in vacuo*. A small amount of chloroform was added and this was washed with a large amount of saturated aqueous sodium chloride. The organic layer was dried (Na_2SO_4), and the solvent removed *in vacuo* again to leave a dark yellow solid (650 mg) which proved to be a mixture containing **3** that was completely inseparable via column chromatography using flash silica gel, Kieselgur G, or neutral alumina. Nor was any separation observed on reverse phase silica. The impurities were identified via NMR and FABMS as vinyl ethers, and so silver nitrate-impregnated TLC plates were made by eluting standard silica TLC plates with 10% aqueous silver nitrate and then leaving them at 120°C for 2 h to activate. However, when these were used, no better separation was observed.

7.5.7. *4,5-Dihydroxy-2-nitrobenzaldehyde (11)* [9]

Aluminium trichloride (35 g, 0.26 mol) was added to dry dichloroethane (105 ml) under argon at −5°C. 6-Nitropiperonal (**10**) (17.5 g, 0.1 mol) was then added in dichloroethane (140 ml). The temperature rose to 20°C temporarily and stirring became impossible, but after a short time the temperature fell to 0°C and stirring was again possible. The reaction mixture was kept at this temperature for 1.5 h and then poured onto cold 48% aqueous HBr (250 ml). After 65 h stirring at room temperature there was still some starting material left so 60% HBr (~30 ml) was added; the reaction mixture was stirred for another 5 h (by which time the reaction had gone to completion) and then water was added. The mixture was shaken with ethyl acetate, the extracts were dried (Na_2SO_4), the solvent was removed *in vacuo* and the residue was dissolved in ethyl acetate and precipitated with petroleum ether to yield the benzaldehyde **11** as a yellow solid (14.5 g, 89%), m.p. 204–205°C (lit. 203–204°C). IR: ν_{max} 3400–3200 (OH stretch), 1700 cm^{-1} (carbonyl stretch). ^{1}H NMR (d_6-acetone) δ 10.25 (s, 1H, ArCHO), 10.06 (broad s, 2H, –OH), 7.61 (s, 1H, proton in the 3-position on the aromatic ring), 7.33 (s, 1H, proton in the 6-position on the aromatic ring). EIMS: *m*/*z* (%) 183 (M^+, 48), 153(100), 136(49), 108(82), 79(59), 51(65).

7.5.8. *4,5-Diacetoxy-2-nitrobenzaldehyde (12)* [9]

Compound **11** (1 g, 6.1 mmol) was stirred for 45 min at 60°C in acetic anhydride (5 ml, 0.053 mol) with sodium acetate (60 mg, 0.7 mmol). The reaction mixture was then poured onto ice and the resulting light brown solid, 4,5-diacetoxy-2-nitrobenzaldehyde **12**, filtered off, washed with cold water, and left in a desiccator (1.4 g, 96%), m.p. 112–114°C (lit. 113°C). ^{1}H NMR ($CDCl_3$) δ 10.42 (s, 1H, ArCHO), 8.25 (s, 1H, proton in the 3-position on the aromatic ring), 7.85 (s, 1H, proton in the 6-position on the aromatic ring), 2.44 (s, 6H, Ar–$(OCOC\underline{H}_3)_2$).

7.5.9. *4,5-Bis[2-(2-methoxyethoxy)ethoxy]-2-nitrobenzaldehyde (**13**)*

Powdered KOH (1.68 g, 29.96 mmol) was mixed with DMSO (15 ml) at room temperature and stirred for 10 min. Compound **12** (2.0 g, 7.49 mmol) was added, followed by 1-bromo-2-(2-methoxyethoxy)ethane (5.48 g, 29.96 mmol), and the reaction mixture was stirred at 55°C for 3 h. The reaction mixture was then filtered through a thin silica gel column using dichloromethane as eluent to remove the excess of KOH and inorganic salts. The organic solution obtained was concentrated and the desired product separated by column chromatography on silica gel as a dark orange oil using ethyl acetate/petroleum spirit (3/1) as solvent (2.32 g, 5.99 mmol, 80%). Found, C 52.65, H 6.55, N 3.50; $C_{17}H_{25}NO_9$ requires C 52.71, H 6.46, N 3.62%. UV (dichloromethane): λ_{max} 264, 310, 346 nm. IR: ν_{max} 1720 cm^{-1} (carbonyl stretch). ^1H NMR ($CDCl_3$) δ 10.45 (s, 1H, ArCHO), 7.72 (s, 1H, proton in the 3-position on the aromatic ring), 7.45 (s, 1H, aromatic proton in the 6-position on the aromatic ring), 4.34 (2xt, $J=7$ Hz, 4H, $ArOCH_2$), 3.91 (2xt, $J=7$ Hz, 4H, $ArOCH_2C\underline{H}_2$), 3.75 (2xt, $J=7$ Hz, 4H, $ArOCH_2CH_2OC\underline{H}_2$), 3.58 (2xt, $J=7$ Hz, 4H, $ArOCH_2CH_2OCH_2C\underline{H}_2$), 3.4 (s, 6H, $-OCH_3$). EIMS: *m*/*z* (%) 387 (M^+, 2), 357(5), 250(23), 158(18), 149(22), 124(35), 109(20), 103(25), 59(100), 43(58).

7.5.10. *5,6-Bis[2-(2-methoxyethoxy)ethoxy]anthranil (**14**)*

Tin powder (8.0 g, 0.067 mol) was added to compound **13** (7.4 g, 0.019 mol) while it was stirred in glacial acetic acid (300 ml). Stirring at room temperature was continued for 7 h when ether was added. The mixture was filtered, and the filtrate washed with water. The organic layer was separated and the aqueous layer shaken with dichloromethane; the combined organic extracts were washed with potassium carbonate solution and then with water, dried (Na_2SO_4) and the solvent removed *in vacuo* to leave a dark red oil. This was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate (1/1) as eluant, increasing the concentration of ethyl acetate with time. The fully alkylated anthranil **14** was isolated as an orange/brown oil (3.9 g, 57%) which was crystallized from petroleum ether/dichloromethane to give yellow/white crystals, m.p. 36–38°C. Found, C 57.4, H 7.05, N 3.9; $C_{17}H_{25}NO_7$ requires C 57.45, H 7.09, N 3.6%. UV (dichloromethane): λ_{max} 282, 294 nm. ^1H NMR ($CDCl_3$) δ 8.8 (s, 1H, proton on the heterocyclic ring), 6.76 (s, 1H, proton in the 7-position), 6.65 (s, 1H, proton in the 4-position), 4.24 (t, $J=7$ Hz, 2H, $ArOCH_2$), 4.13 (t, $J=7$ Hz, 2H, $ArOCH_2$), 3.91 (2xt, $J=7$ Hz, 4H, $ArOCH_2C\underline{H}_2$), 3.75 (2xt, $J=7$ Hz, 4H, $ArOCH_2CH_2OC\underline{H}_2$), 3.6 (2xt, $J=7$ Hz, 4H, $ArOCH_2CH_2OCH_2C\underline{H}_2$), 3.4 (s, 6H, $-OCH_3$). EIMS: *m*/*z* (%) 355 (M^+, 32), 177(11), 151(9), 103(42), 59(100), 45(26).

7.5.11. *2,3,7,8,12,13-Hexakis[2-(2-methoxyethoxy)-ethoxy]tricycloquinazoline (**3**)*

Ammonium acetate (6 g, excess) was added to a stirred mixture of the anthranil **14** (2 g, 5.9 mmol) in glacial acetic acid (35 ml) under nitrogen at 110°C. The reaction mixture was stirred at this temperature for 67 h and then poured into water. The mixture was shaken with dichloromethane and the extracts were washed with potassium carbonate solution and with water, dried (Na_2SO_4), and the solvent was removed *in vacuo* to leave a dark red oil. The trimer **3**, was isolated via column chromatography on silica gel using dichloromethane/methanol (4/96) as eluant, and then crystallised and recrystallised from dichloromethane/ether to yield a yellow solid (360 mg, 18%); transition temperatures: Cr (77°C) Col_h (233°C) I. Found, C 59.52, H 7.10, N 5.40; $C_{51}H_{72}N_4O_{18}$ $1/2H_2O$ requires C 59.50, H 7.08, N 5.40%. UV (dichloromethane): λ_{max} 266, 277, 300, 315, 369, 391, 416 nm. ^1H NMR ($CDCl_3$) δ 7.68 (s, 3H, aromatic protons in the 4-, 9- and 14-positions), 6.86 (s, 3H, aromatic protons in the 1-, 6- and 11-positions), 4.3 (t, $J=7$ Hz, 12H, $Ar{-}OCH_2$), 3.95 (t, $J=7$ Hz, 12H, $Ar{-}OCH_2C\underline{H}_2$), 3.8 (t, $J=7$ Hz, 12H, $Ar{-}OCH_2CH_2OC\underline{H}_2$), 3.62 (t, $J=7$ Hz, 12H, $Ar{-}OCH_2CH_2OCH_2C\underline{H}_2$), 3.45 (s, 18H, $O{-}CH_3$). FABMS: *m*/*z* (%) 1030 (M^+, 100), 997(6), 926(13), 824(7).

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