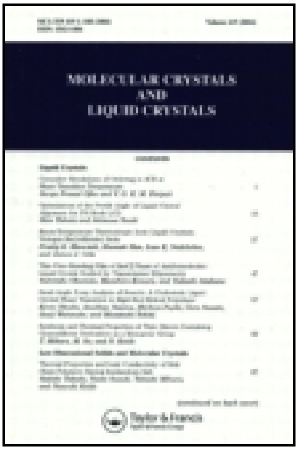

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Cyclic Voltammetry Studies of Discotic Liquid Crystals

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CYCLIC VOLTAMMETRY STUDIES OF DISCOTIC LIQUID CRYSTALS

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The first oxidation (reduction) potentials have been measured by cyclic voltammetry for twenty-five different triphenylene based discotic liquid crystals and related systems. The measured potentials correlate reasonably well with values calculated at the PM3 level and can be understood in terms of substituent effects. There is a substantial difference between the oxidation potentials of the components in mixed CPI systems; a surprising finding in view of their high hole mobilities. For 2,3,7,8,12,13-hexakis(2-(2′-methoxyethoxy)-ethoxy) tricycloquinazoline both CV and NMR show that there is aggregation in acetonitrile solutions.

Keywords: cyclic voltammetry; discotic liquid crystals; organic semi-conductors; redox potentials; semi-empirical calculation

INTRODUCTION

Columnar liquid crystals are an exciting class of semi-conducting materials which are self-organising and self-healing with a variety of potential applications [1]. Since there is a poor match between the work-functions of most commonly available metals and the redox potentials of most readily available discotic liquid crystals there is an intrinsic barrier to charge injection at the DLC/Metal interface [2]. Provided the liquid crystal is free from ionic impurities no current can flow in the Metal|DLC|Metal cell until this barrier is overcome (Fig. 1). Hence a knowledge of the redox potentials of liquid crystals is important to further our understanding of conduction in these

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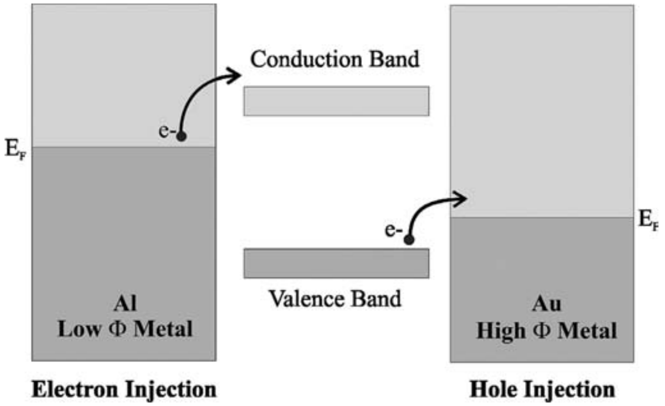

FIGURE 1 Representation of the energy band diagram for a Metal|DLC|Metal cell.

systems. In this paper we report the redox potentials of a variety of functionalised triphenylene based discogens as determined by cyclic voltammetry and semi-empirical MO calculations.

EXPERIMENTAL

Materials

The syntheses of the discogens shown in Figure 2 have been previously described [3]. HPLC grade dichloromethane was supplied by Riedel-de Haen and was distilled from calcium hydride prior to use. HPLC grade benzonitrile from Sigma-Aldrich was used as supplied. Acetonitrile supplied by Fisher Scientific was dried over alumina and distilled prior to use. Tetrabutylammonium hexafluorophosphate (TBA-HFP) and ferrocene from Sigma-Aldrich were used as supplied.

Cyclic Voltammetry

Cyclic voltammetry was carried out using an EG&G model 362 scanning potentiostat controlled by a personal computer running EG&G CONDECON software. A conventional three-electrode cell was used consisting of a 1 mm diameter platinum disc electrode, a silver-silver chloride reference electrode and a platinum wire counter electrode. The reference electrode consisted of a silver wire suspended in the electrolyte solution saturated with lithium chloride. Dichloromethane and benzonitrile were used as solvents with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Sweep rates of 500, 200,100 and 50 mVs^{-1} were used. A mean in the measured redox potential was taken over five sweeps. Experimental error was estimated to be $<20\,\text{mV}$. Before each measurement the solution was purged with dry argon to ensure an oxygen-free environment. All experiments were carried out at ambient temperature. The data were processed using the CONDECON software. Deconvolution (derived from convolution or semi-integral analysis) methods were applied via the derivative of the semi-integral (I_1 convolution) with respect to potential. These allowed greater accuracy in determining the potentials of interest and allowed easy assessment of the electrochemical 'reversibility' of the reactions i.e., whether the measured potential reflects the concentrations at the electrode via the Nernst relationship [4]. The measured potentials were corrected to an internal ferrocene standard, which was assumed to have an oxidation potential of $+0.51\,\text{V}$ versus silver-silver chloride in the electrolyte used.

MO Calculations

Semi-empirical calculations at the PM3 level were performed using Hyperchem 5.0 Professional [5]. Molecular geometries for the methoxy or methyl substituted model discogens were optimised using a conjugate gradient method with a convergence limit of $0.01\,\text{kcal}\,\text{Å}^{-1}\text{mol}^{-1}$. To obtain more accurate ionisation energies a single point semi-empirical calculation was performed with a singly excited orbital criterion configuration interaction (CI) using three occupied and three unoccupied orbitals. After the initial geometry and energy of the neutral model discogen was determined, the process was repeated with one electron removed from the SCF calculation to obtain an estimate for the energy of the charged (hole-bearing) system. The ionisation potential E_{MO} was calculated as the difference between the energies of the neutral and ionised species.

RESULTS AND DISCUSSION

Most discotic liquid crystals have π-excessive aryl cores and are hole transporters. Only a few, like TCQ **6**, are effective electron transporters [6]. The structures of the discotic liquid crystals studied are shown in Figure 2 and the measured redox potentials (E_{CV}) versus Ag/AgCl are given in Table 1 together with ionisation energies calculated by the semi-empirical PM3 method (E_{MO}). Figure 3 shows, the deconvolution CV results via $\mathrm{dI_1/dE}$ for HAT6. The peak width is close to the theoretical value of $90\,\text{mV}$ for a reversible single electron oxidation. The reduction peak is the mirror image of the oxidation peak, demonstrating the chemical reversibility of the reaction. In most cases there were no significant

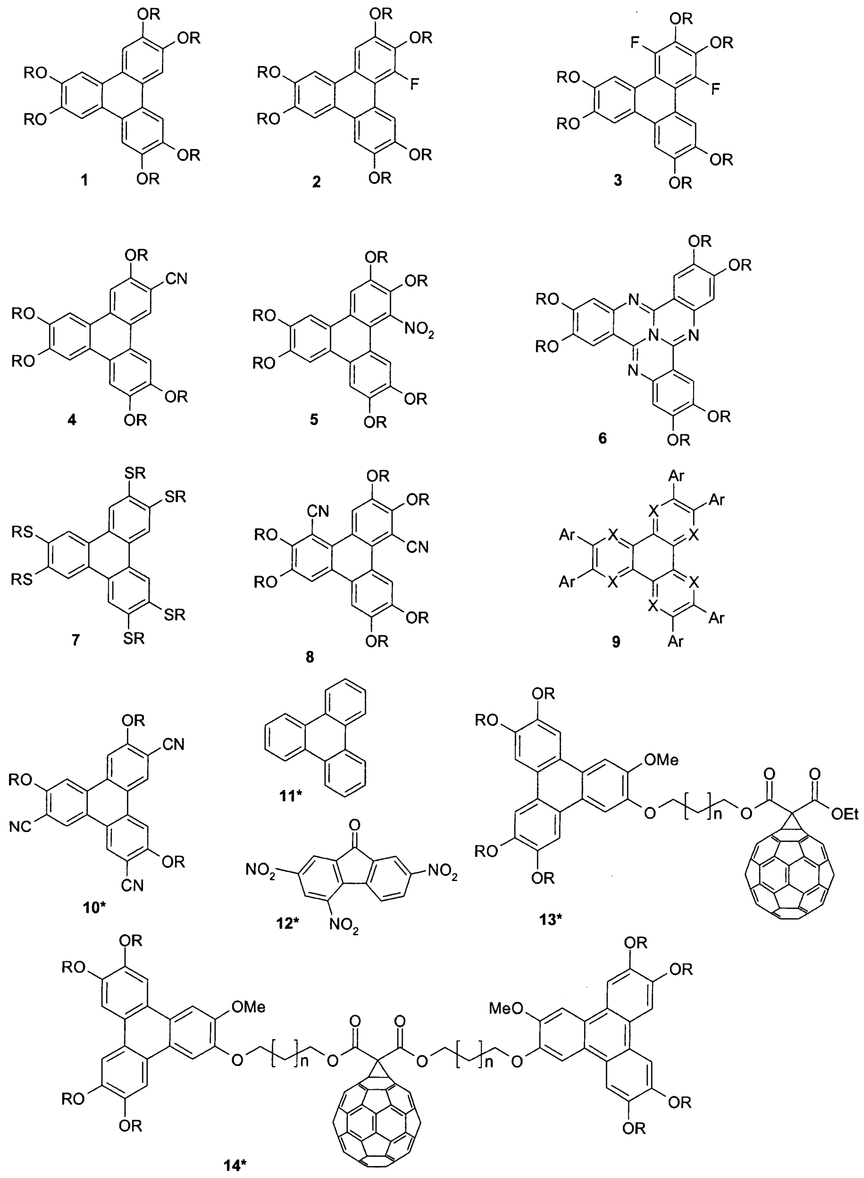

FIGURE 2 HATn **1** (**1a** R=C_2H_5, **1b** R=C_3H_7, **1c** R=C_6H_{13}, **1d** R=C_8H_{17}, **1e** R=$C_{10}H_{21}$, **1f** R=$C_{12}H_{25}$, **1g** R=$C_{14}H_{29}$, **1h** R=$C_{16}H_{33}$) [8-10]; **2** [11], **3** [12], **4** [9,13,14], **7** [15], **8** [14], **10** [9,13,14], **13** [16], **14** [16] R=C_6H_{13}; **5** (**5a** R=C_3H_7, **5b** R=C_7H_{15}, **5c** R=C_8H_{17}, **5d** R=$C_{10}H_{21}$, **5e** R=$C_{12}H_{25}$) [10,11]; **6** R=$((CH_2)_2O)_2CH_3$ [6]; PTP **9** (**9a** X=CH Ar=C_6H_4–OC_6H_{13}, **9b** X=CH Ar=C_6H_4–C_9H_{19}, **9c** X=N Ar=C_6H_4–C_9H_{19}) [17,18]. *Non-mesogenic.

TABLE 1 Experimental and Calculated Potentials for the Molecules Listed in Figure 2

Compound	Reduction potential (V)*	Oxidation potential (V)*	E_{MO} (eV)†	Solvent	Reversibility
1a	1.08	$<-0.6^{\ddagger}$	7.67	CH_2Cl_2	Reversible
1b	1.07	<-0.6	7.67	CH_2Cl_2	Reversible
1c	1.08	<-0.6	7.67	CH_2Cl_2	Reversible
1d	1.09	<-0.6	7.67	CH_2Cl_2	Reversible
1e	1.07	<-0.6	7.67	CH_2Cl_2	Reversible
1f	1.20	<-0.6	7.67	CH_2Cl_2	Reversible
1g	1.08	<-0.6	7.67	CH_2Cl_2	Reversible
1h	1.04	<-0.6	7.67	CH_2Cl_2	Reversible
2	1.12	<-0.6	7.68	CH_2Cl_2	Reversible
3	1.16	<-0.6	7.72	$PhCH_2CN$	Semi reversible
4	1.17	<-0.6	7.83	$PhCH_2CN$	Semi reversible
5a	1.22	<-0.6	7.77	CH_2Cl_2	Reversible
5b	1.22	<-0.6	7.77	CH_2Cl_2	Reversible
5d	1.24	<-0.6	7.77	$PhCH_2CN$	Reversible
5e	1.27	<-0.6	7.77	$PhCH_2CN$	Reversible
6	1.20	<-0.6	7.85	CH_3CN	Semi reversible
7	1.28	<-0.6	7.89	CH_2Cl_2	Semi reversible
8	1.40	<-0.6	7.99	$PhCH_2CN$	Semi reversible
9a	1.56	<-0.6	7.96	$PhCH_2CN$	Semi reversible
9b	1.50	<-0.6	7.96	$PhCH_2CN$	Semi reversible
9c	$>1.80^{\ddagger}$	<-0.6	8.56	$PhCH_2CN$	Semi reversible
10	1.73	<-0.6	8.44	$PhCH_2CN$	Semi reversible
11	1.79	<-0.6	8.37	$PhCH_2CN$	Semi reversible
12	$>1.4^{\ddagger}$	-0.09, -0.41	–	CH_2Cl_2	Reversible
13	1.05	-0.42	7.67	$PhCH_2CN$	Semi reversible
14	1.01	-0.45	7.67	$PhCH_2CN$	Semi reversible

*±0.02 V Pt working electrode vs Ag/AgCl reference, 0.1 M TBA-HFP. †PM3 calculations using 3 × 3 CI. ‡Limit of the solvent accessible window.

differences between first and subsequent sweeps confirming the absence of chemical processes on the timescales employed. The potentials obtained for the hexaalkoytriphenylene nucleus agree with the values previously obtained under these conditions [7].

For most of these materials, only the potential of the first oxidation process falls within the experimentally accessible window, which is limited by the electrolyte medium. The experimental trends in this potential are more-or-less as expected for oxidation of the triphenylene molecule. They are lowered by adding electron donating alkoxy substituents (compare **1** and **10**) and increased by addition of electron withdrawing groups such as F, CN, and NO_2 (compare **2**, **4** and **5**). This effect is compounded when more than one electron withdrawing group is present (compare **2** with **3** or

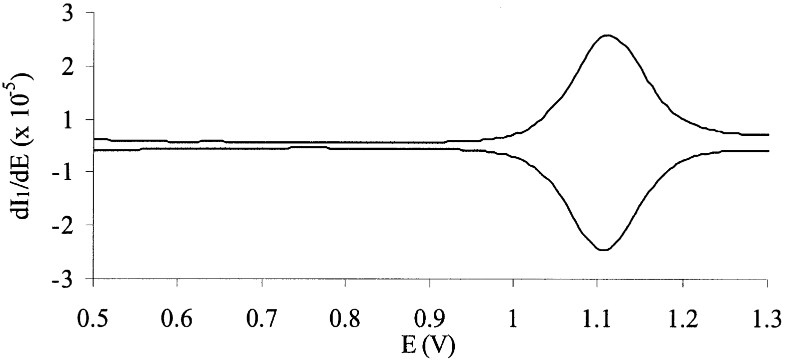

FIGURE 3 dI_1/dE CV data for HAT6 **1c** in dichloromethane vs Ag/AgCl reference.

4 with **10**). The potential at which the oxidation process occurs is essentially a property of the electrophore (the aromatic/hetrocyclic nucleus) and is not affected (within experimental error) by the length of the sidechains (compare **1a-h** and **5a-e**). Figure 4 shows a comparison of measured oxidation potentials by cyclic voltammetry (E_{CV}) and calculated ionisation potentials (E_{MO}). There is an almost linear relationship between the E_{CV} and E_{MO}. The relationship between the values is approximately given by:

$$E_{MO} = aE_{CV} + \sum b_i,$$

where Σb_i denotes solvation, reorganisation and configurational interaction energies [19]. Despite the fact that some of the data were obtained in acetonitrile and some in dichloromethane, there is a reasonably good correlation between E_{MO} and E_{CV}.

The mesophase range of hexaalkoxytriphenylene discotics HATn **1** can be enhanced by adding TNF **12** or one of the substituted hexaphenyltriphenylenes (PTP) **9** [17, 20]. In both cases it is believed that alternating mixed columnar stacks are formed. A charge transfer band is observed in mixtures of HAT **1** with TNF **12**, but in the binary mixtures of PTP **9** with HATn **1**, the UV/Visible spectra are unchanged. According to the cyclic voltammetry measurements, HAT **1** and TNF **12** have a difference in redox potentials of 1.17 V but in the case of HAT **1** with PTP **9** it is greater than 1.53 V making charge-transfer more difficult. In the former case the enhanced mesophase range has been ascribed to the charge transfer interaction or net quadrupolar interactions but in mixtures of HAT **1** and PTP **9** the observed increase in stability of the mesophase cannot be explained in this way [21].

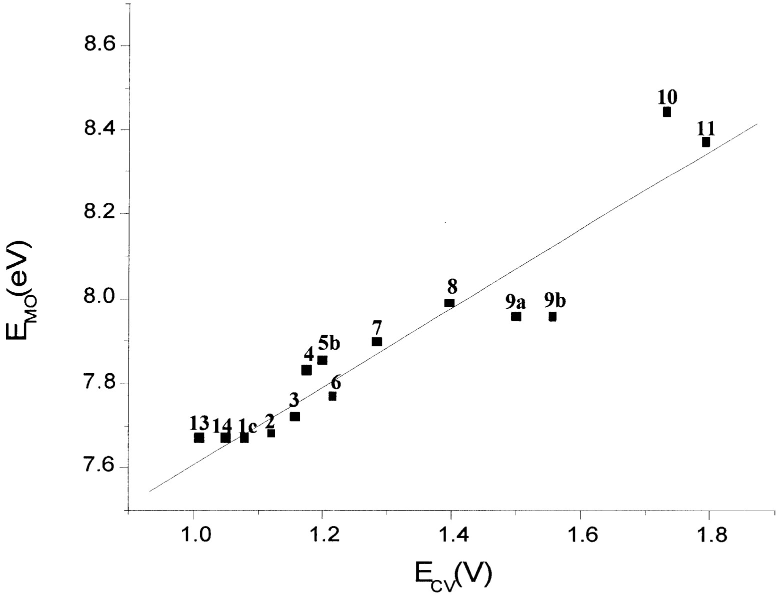

FIGURE 4 Correlation between the first oxidation potentials determined by cyclic voltammetry (E_{CV}) and the ionisation potentials calculated by the PM3 method (E_{MO}).

For the binary 1:1 mixture of HAT6 **1c** and PTP9 **9b** mobilities of 2.3×10^{-2} and $1.4 \times 10^{-2}\,cm^2V^{-1}s^{-1}$ were obtained from TOF photoconduction measurements in the mesophase and glassy phases respectively [22]. This compares with a mobility of $7.4 \times 10^{-4}\,cm^2V^{-1}s^{-1}$ for HAT6 in the mesophase. The difference in oxidation potentials between HAT6 **1c** and PTP9 **9b** (0.42 V) presents a barrier to charge carrier transport. A hole migrating along the stack will experience a strongly alternating potential, but this is overcome by the relatively large bandwidth found in these mixtures [23].

For most cases shown in Table 1 the width at half-height in the dI_1/dE cyclic voltammetry plot was close to the theoretical value of 90 mV for single electron transfer and well-shaped peaks were observed like those shown in Figure 3. For 2,3,7,8,12,13-hexakis(2-(2′-methoxyethoxy) ethoxy)tricycloquinazoline (TCQ) **6** in acetonitrile, however, complex peak shapes were obtained with total widths between 162 and 325 mV depending on the concentration (between 0.26 mM and 3.10 mM). This is attributed to aggregation. Typical dI_1/dE cyclic voltammetry plots obtained in dichloromethane and acetonitrile and a plot of the overall peak width as a function of concentration are shown in Figure 6. As the concentration

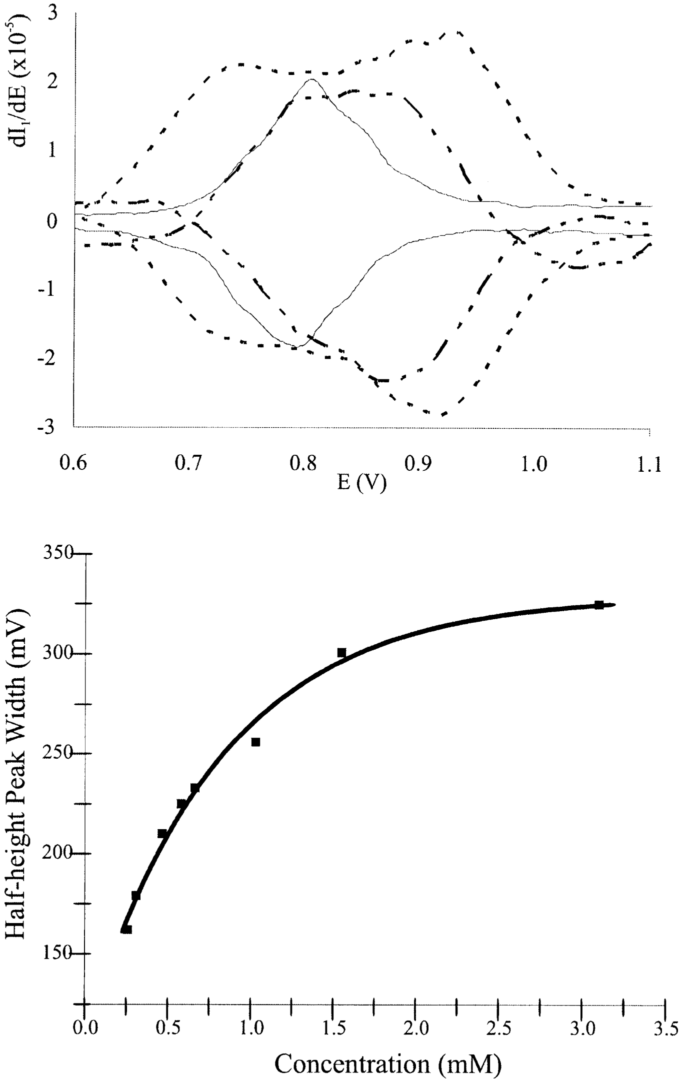

FIGURE 5 Top shows dI_1/dE CV data for 2,3,7,8,12,13-hexakis(2-(2′-methoxyethoxy)ethoxy)tricycloquinazoline (TCQ) **6** at a sweep rates of 50 mV/s versus a silver/silver chloride reference electrode; dotted line = 3.1 mM in acetonitrile, dashed line = 0.31 mM in acetonitrile, solid line = 0.22 mM in dichloromethane. Bottom shows peak width at half-height for TCQ **6** in acetonitrile as a function of concentration.

is lowered the size of the aggregates and distribution of aggregate sizes decreases leading to narrower peaks. If the molecules or charges in TCQ aggregates were not interacting we would expect to get a simple CV wave with a peak width of 90 mV (regardless of the size of the aggregate). The fact that we get a wide peak with a complex shape shows that there is interaction between the charges and/or banding along the aggregates. In dichloromethane TCQ **6** is monomeric and the expected peak width of ~90 mV is observed.

Further evidence for the aggregation in acetonitrile in this concentration range is provided by ^{1}H-NMR spectroscopy (Fig. 7). At a concentration of

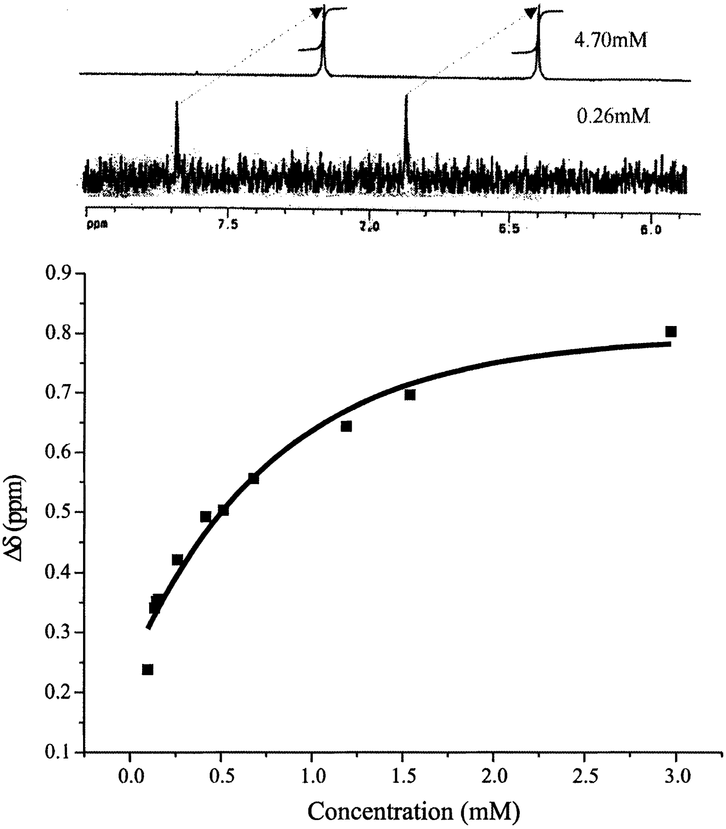

FIGURE 6 Top shows ^{1}H-NMR spectra for TCQ **6** in d_3-acetonitrile at high and low concentrations at room temperature. Bottom shows chemical shift difference ($\Delta\delta$/ppm) for the low field aromatic proton as a function of concentration for TCQ **6** in d_3-acetonitrile at room temperature.

0.26 mM in d_3-acetonitrile solution and 18°C (or in $CDCl_3$ in which monomers also dominate) the resonances due to the protons of the aromatic core occur at 7.68δ and 6.86δ. At 4.70 mM in d_3-acetonitrile solution and 18°C (where aggregates dominate) these resonances are shifted downfield to 6.43δ and 7.20δ.

This can be attributed to long range shielding resulting from the ring currents of the aryl rings stacked one-on-top of the other. The fact that TCQ **6** gives columnar aggregates in water [6] is not surprising since it is analogous to the behaviour of 2,3,6,7,10,11-hexakis(2-(2′-methoxyethoxy)-ethoxy)triphenylene in water [24]. The formation of similar aggregates in acetonitrile is more surprising.

CONCLUSIONS

Values of the redox potentials are important to our understanding of conduction in discotic liquid crystals. The values obtained by cyclic voltammetry correlate well with the ionisation potentials obtained by semi-empirical calculations, which increases confidence in using these methods where experimental values are not available. There are few surprises in the general trends in the values obtained except that there is such a large difference in oxidation potentials of the two components of the mixed ‘CPI’ stacks; particularly in view of the high hole mobilities in these systems. The other surprising result was the discovery of aggregation of TCQ **6** in acetonitrile. It holds out the interesting prospect of using CV to probe aggregation in this and other discogenic systems.

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