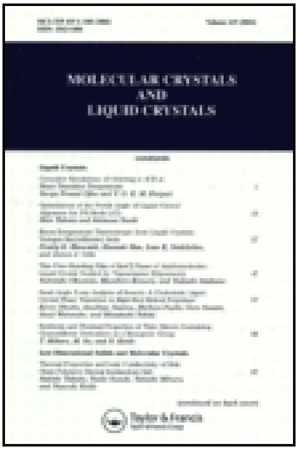

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Electroluminescent Liquid Crystals

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Electroluminescent Liquid Crystals

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A new class of liquid crystals for use as transport layers and/or emission layers in organic light-emitting diodes has been prepared. Depending on the nature and number of the terminal substituents enatiotropic nematic, smectic and columnar phases are observed. Chain branching gives rise to materials with a low melting point. Several of these liquid crystals electroluminesce in the visible region. The charge transport properties of some of these materials have been evaluated.

Keywords: light-emitting organics; OLEDs; nematics

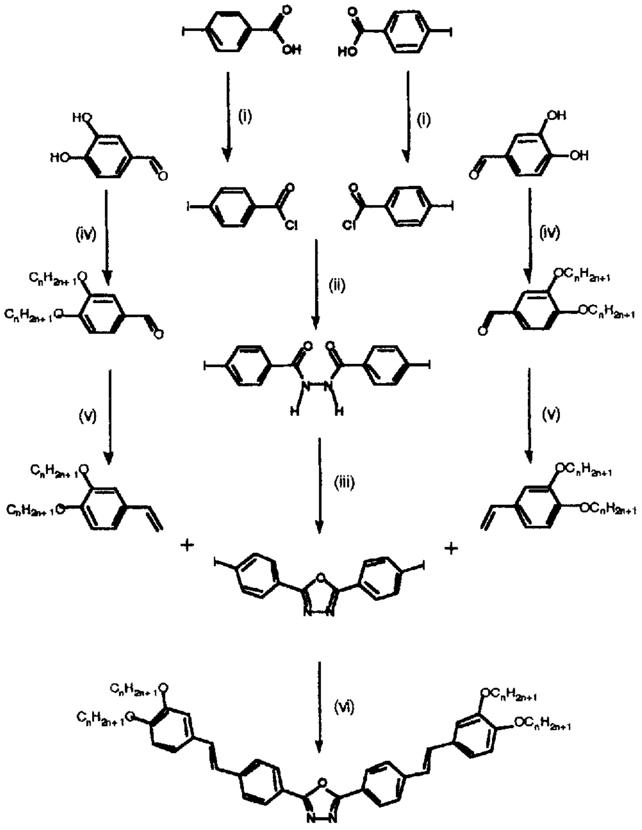
INTRODUCTION

It was recently reported that triphenylenes [1-6] and phthalocyanines [7-9] could exhibit large charge mobility in the columnar (discotic) liquid crystalline state. The values observed in the ordered hexagonal columnar phase of *hexakis*(*n*-alkoxy)triphenylenes and in the helical columnar phase of the hexakis(*n*-alkylthio)triphenylenes [4] for the charge carrier mobility (10^{-1} cm^{2}V^{-1}s^{-1} > μ_h > 10^{-3} cm^{2}V^{-1}s^{-1}) are intermediate between those observed for organic single crystals and inorganic semiconductors ($\mu \approx 1$ cm^{2}V^{-1}s^{-1}) and those (10^{-3} cm^{2}V^{-1}s^{-1} > μ > 10^{-6} cm^{2}V^{-1}s^{-1}) of amorphous conjugated polymers, *c.f.* poly(*N*-vinylcarbazole, (PVK). The majority charge carrier are holes, rather than electrons, due to the very limited electron affinity and low ionisation potential of the electron-rich aromatic cores of this kind of columnar liquid crystals. The charge transport is non-dispersive. Therefore, the charge carrier mobility parallel to the director, i.e. parallel to the core of the columns of self-assembled disks, is orders of magnitude higher than that measured orthogonal to the director, i.e. from column to column. This is attributable in part to the insulating nature of the lateral aliphatic chains surrounding the aromatic cores.

Hence, columnar (discotic) liquid crystals with an aromatic central core[1-14] are of significant potential interest for application in Organic Light-Emitting Diodes (OLEDs) as a hole transport layer,as long as the columnar phase can be aligned with the columns orthogonal to the substrate surface, i.e. the flow of holes from the anode to the ETL and/or emission layer is facilitated. Columnar liquid crystals generally consist of disc-shaped molecules or self-assembled aggregates organised in a supramolecular structure of nearly parallel columns of varying degrees of order in a two-dimensional lattice.[8-12] The largest values for mobility ($\mu \approx 4 \times 10^{-1}$ cm^2 V^{-1} s^{-1}) have been found for columnar liquid crystals with large polyaromatic cores, such as coronenes.[13] However, the very high clearing point often found for such columnar liquid crystals renders them very difficult to align by cooling from the isotropic liquid into the column phase followed by annealing in the columnar state. Polycatenar compounds, with more than one terminal chain at each end of a rod-like molecule, can also exhibit columnar phases, although they possess a linear molecular structure.[16] Three linear molecules can self-assemble and aggregate together to form a disk, which then stacks up with other disks to form a fluid columnar structure. However, a potential problem associated with the practical fabrication of multilayer OLEDs with low-molar-mass columnar liquid crystals a charge-transport layer, especially as the lower hole transport layer, is the fluid nature of the liquid crystalline state. This could result in contamination of the columnar liquid crystal during the deposition of subsequent layers by the process of vapour deposition or spincoating, since the columnar material could well be soluble in the solvent used to deposit the next layer. Therefore, crosslinked networks have recently been prepared in order to address this problem[17]. In this case rod-like photopolymerisable electroluminescent liquid crystals have also been macroscopically aligned in the nematic state and then the order frozen in by photochemical polymerissation. This gives rise to stable insoluble polymer networks. These can be use to fabricate multilayer OLEDs, especially with polarised emission. This approach should also be applicable to columnar and clamitic liquid crystals as the hole transport layer.

SYNTHESIS

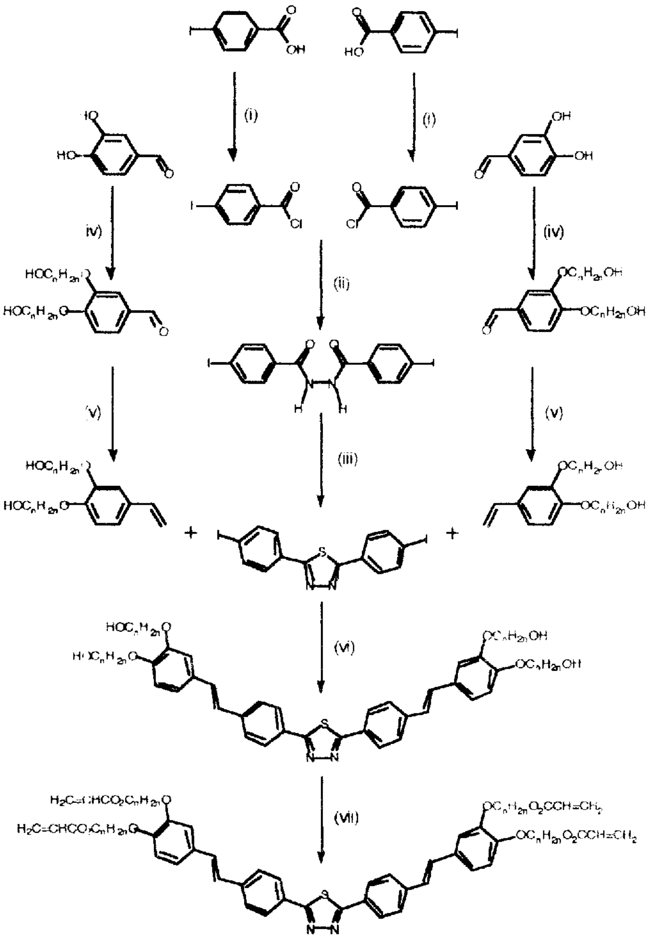
The 2,5-bis(4-[(*E*)-2-(3,4-dialkoxyphenyl)ethenyl]phenyl)oxadiazoles **1-8** were prepared as shown in reaction scheme 1. 4-iodobenzoic acid was converted into the acid chloride using thionyl chloride. This was reacted with hydrazine hydrate to form a symmetrical diamide. This is converted to the oxadiazole using phophorous pentoxide. A Heck reaction using the 3,4-dialkoxystyrene yields the final products **1-8**. The 3,4-dialkoxystyrene was prepared from 3,4-dialkoxybenzaldehyde, prepared by alkylation of commercially available 3,4-dihydroxybenzaldehyde. The corresponding compounds **9-16** were synthesised analogously using 3,4,5-trihydroxybenzaldehyde.



(i) $SOCl_2$
(ii) $H_2N.NH_2$/THF
(iii) $POCl_3$ or P_4S1_0
(iv) BrC_nH_{2n+1}/K_2CO_3/$CH_3COC_2H_5$
(v) $CH_3P(C_6H_5)_3Br$/$KOC(CH_3)_3$/DME
(vi) $Pd(O_2CCH_3)_2$/(o-$CH_3C_6H_5$/$N(C_2H_5)_3$

Scheme 1

The photopolymerisable tetraacrylate **17** was prepared in a similar fashion as shown in reaction scheme 2.



(i) $SOCl_2$; (ii) $H_2N.NH_2$/THF; (iii) P_4S1_0; (iv)BrC_nH_{2n+1}/K_2CO_3/$CH_3COC_2H_5$;
(v) $CH_3P(C_6H_5)_3Br$/$KOC(CH_3)_3$/DME; (vi) $Pd(O_2CCH_3)_2$/(o-$CH_3C_6H_5$/$N(C_2H_5)_3$;
(vii) H_2C=$CHCO_2H$/DCC/DMAP/CH_2Cl_2

Scheme 2

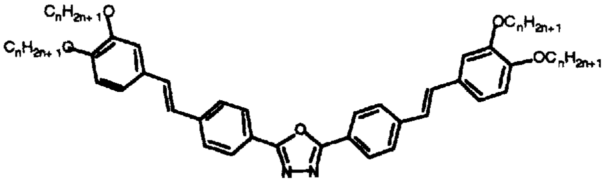
RESULTS AND DISCUSSION

The liquid crystal transition temperatures of the polycatenar compounds **1-8** are collated in Table 1. The melting point decreases with increasing alkoxy chain length from very high values for the shortest chains studied (n = 2 and 4). Therefore, the first two homologues of the series do not exhibit any observable liquid crystalline phases. However, an enantiotropic smectic C phase is found for compounds with intermediate chain lengths (n = 6 and 8). This phase is then replaced by an enantiotropic columnar phase for long alkoxy chains (n > 9). Optical microscopy suggests that this phase is a hexagonal columnar phase.

The thermal date for the analogous hexacatenar compounds **9-16** are listed in Table 2. The presence of the additional two alkoxy chains results in much lower melting points than those observed for the corresponding tetracatenar compounds **1-8**. However, the first three members (n = 2, 4 and 6) of the series studied are mot mesomorphic. Moreover, a columnar phase is observed for compounds with an intermediate to long chain (n > 7). The presence of the two additional chains will favour the formation of a columnar aggregate involving three polycatenar molecules to form an hexagonal structure. The clearing point of these homologues is remarkably independent of chain length. A melting point has yet to be determined for compound **14**, which forms a glass at low temperatures by DSC. The photopolymerisable compound **17** exhibits an enantiotropic columnar phase and could be used to form stable and insoluble transport layers in OLEDs.

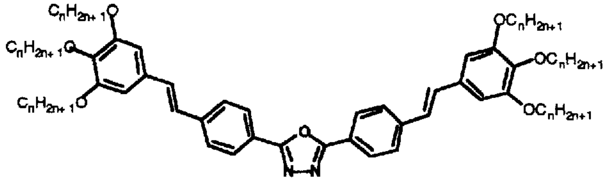
The liquid crystalline temperatures of a series of polyaromatic compounds **18-23** containing at least six phenylene rings are collated in Table 3. The dicatenar perylene compound **18** exhibits a monotropic nematic phase. The presence of more alkoxy chains in the analogous tetracatenar and hexacatenar compounds **19** and **20** results in lower melting point, but also in the suppression of any observable liquid crystalline behaviour. The replacement of a vinylene linkage by a phenylene ring in compound **21** in the table results in a much higher clearing point and a broad enantiotropic nematic phase. The anthracene core of compound **22** is probably too broad to allow liquid crystal phase formation. However, the fluorene **23** possesses an enantiotropic nematic phase. The presence of the two propyl substituents at position 9 on the fluorene moiety does not interfere with the planarity or the degree of conjugation of the aromatic core. However, the two propyl lateral substituents lower the melting point and increase the solubility of such compounds significantly. All of the compounds in Table 3 emit blue photoluminescent and electroluminescent light. Photopolymerisable versions of the fluorene **23**, with polymerisable endgroups at the end of the alkoxy chains, are in preparation and could be used to generate polarised emission on an appropriate alignment layer. The PL quantum yield of of polyaromatic compounds **18-23** is highest (65%) for the fluorene **23**.

TABLE 1. Transition temperatures (°C) for the compounds below:



Compound	n	Cr		Col		SmC		I
1	2	•	186	-			-	•
2	4	•	150	-			-	•
3	6	•	121	-		•	122	•
4	8	•	108	-		•	120	•
5	10	•	86	•	112			•
6	12	•	90	•	128		-	•
7	14	•	98	•	130		-	•
8	16	•	98	•	139		-	•

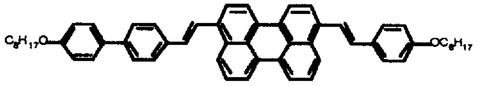
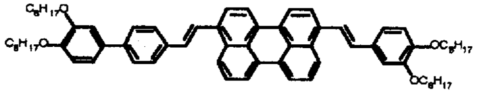
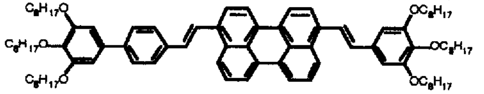
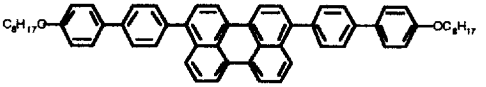
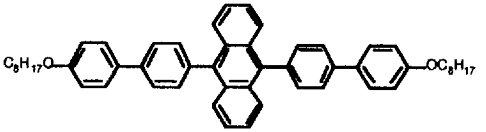
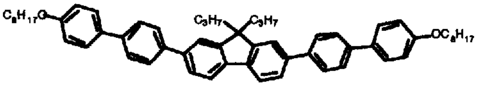
TABLE 2. Transition temperatures (°C) for the compounds below:



Compound	n	Cr		Col		I
9	2	•	125		-	•
10	4	•	165		-	•
11	6	•	118		-	•
12	8	•	88	(•	77)	•
13	9	•	77	•	86	•
14	10	•	-31	•	80	•
15	12	•	78	•	83	•
16	14	•	81	•	83	•

( ) Represents a monotropic transition temperature

TABLE 3. Transition temperatures (°C) for the compounds **18-23** below:

Compound	Cr		N		I
	•	180	(•	173)	•
	•	88		-	•
	•	oil		-	•
	•	183	•	282	•
	•	243		-	•
	•	157	•	232	•

CONCLUSIONS

A number of electroluminescent liquid crystals have been prepared. Polycatenar compounds with a long rod-like molecular core and four or six long terminal chains form columnar phases. Heacatenar compounds exhibit lower transition temperatures than thos eof analogous materials with fewer chains. Photopolymerisable analogues of these new classes of organic materials have been prepared or are in the process of preparation. They will be used for in OLEDs as emission layers for polarised EL or as charge-transport layers.

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