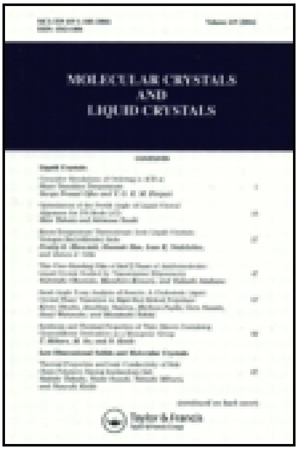

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Synthesis of New Functionalized Discotic Liquid Crystals for Photoconducting Aplications

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SYNTHESIS OF NEW FUNCTIONALIZED DISCOTIC LIQUID CRYSTALS FOR PHOTOCONDUCTING APPLICATIONS

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Abstract The columnar structure of discotic liquid crystals has been shown to be well suited for electronic transport parallel to the columnar axis. To tailor the processibility and mesophase behavior of such materials, several hydroxytriphenylene derivatives were synthesized. These hydroxytriphenylenes can be converted into oligomers, networks or polymers. Further, they can be reduced to arenes which posses reactive sites for classical aromatic substitutions. A number of mixed tail triphenylene derivatives and fluorescent, low symmetry triphenylene discotic liquid crystals were synthesized and characterized.

INTRODUCTION

The supramolecular assemblies of disc shaped molecules lead to the formation of discotic liquid crystals.[1] Though this new class of liquid crystal was discovered eighteen years ago,[2] their potential uses in opto-electronic applications have only recently been sought. The hexagonal ordered phase (D_{ho}) of discotics is well suited for the study of one-dimensional energy transfer.[3] Electrical conductivity in p-doped and n-doped discotics has been studied extensively.[4,5] Discotic liquid crystals have also been found potential uses in other applications such as photovoltaic cells,[6] optical data storage,[7] light emitting diodes,[8] and ferroelectric switching.[9,10]

Triphenylene discotic liquid crystals have recently emerged as a new class of fast photoconducting materials which can be utilized in devices like copying machines and laser printers. Charge carrier mobility of 1×10^{-3} $cm^2v^{-1}s^{-1}$ (hole mobility) has been observed in the ordered columnar phase (D_{ho}) of hexapentyloxytriphenylene (HPT) and a dimer derived from the same molecule,[11,12] exceeding the values for commonly used photoconducting polymers by two or three orders of magnitude. An extremely high charge carrier mobility, comparable to organic single crystals (1×10^{-1} $cm^2v^{-1}s^{-1}$), has been found in the helical phase of hexahexylthiotriphenylene (HHTP).[13] This enhanced photoconductivity has been attributed to long range order occurring along the columns of the helical phase. Clearly, the gross structure of the supramolecular assembly plays a crucial role in the photoconductivity of these systems.

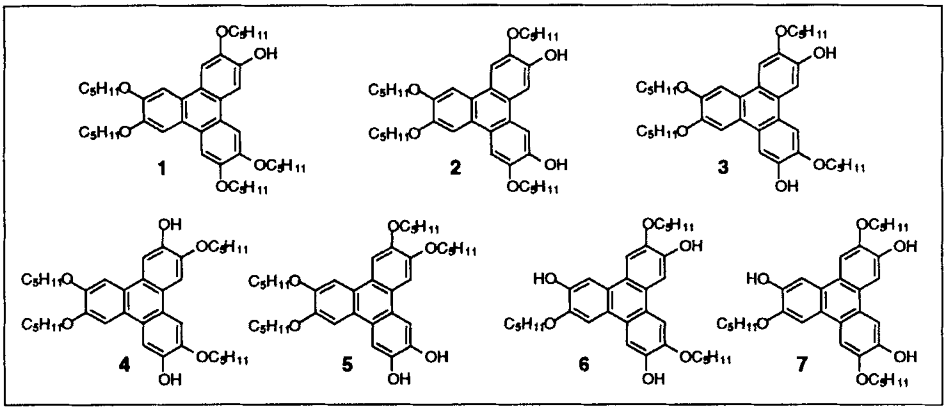
For liquid crystal device purposes, besides molecular stability, the supra molecular structure of the desired mesophase must be thermodynamically stable over a broad temperature range above and below room temperature. The molecular engineering towards more advanced discotic triphenylenes started with the preparation of discotic main chain and side chain polymers[14,15] leading to enhanced mesophase stability and mechanical properties. The synthesis has been achieved by partial hydrolysis/alkylation of triphenylene hexaacetate followed by polymarization and requires tedious separation of products. Thus, we initiated a synthetic program with the objectives -

1. Development of networks to improve the stability of the mesophase and to have a processible material.
2. Preparation of new low molecular mass compounds having more ordered mesophases and thus a higher charge carrier mobility and
3. Synthesis of fluorescent, low symmetry triphenylene discotic liquid crystals especially to study one-dimensional energy migration[3] and LEDs .[16]

SYNTHESIS OF FUNCTIONALIZED TRIPHENYLENE DERIVATIVES

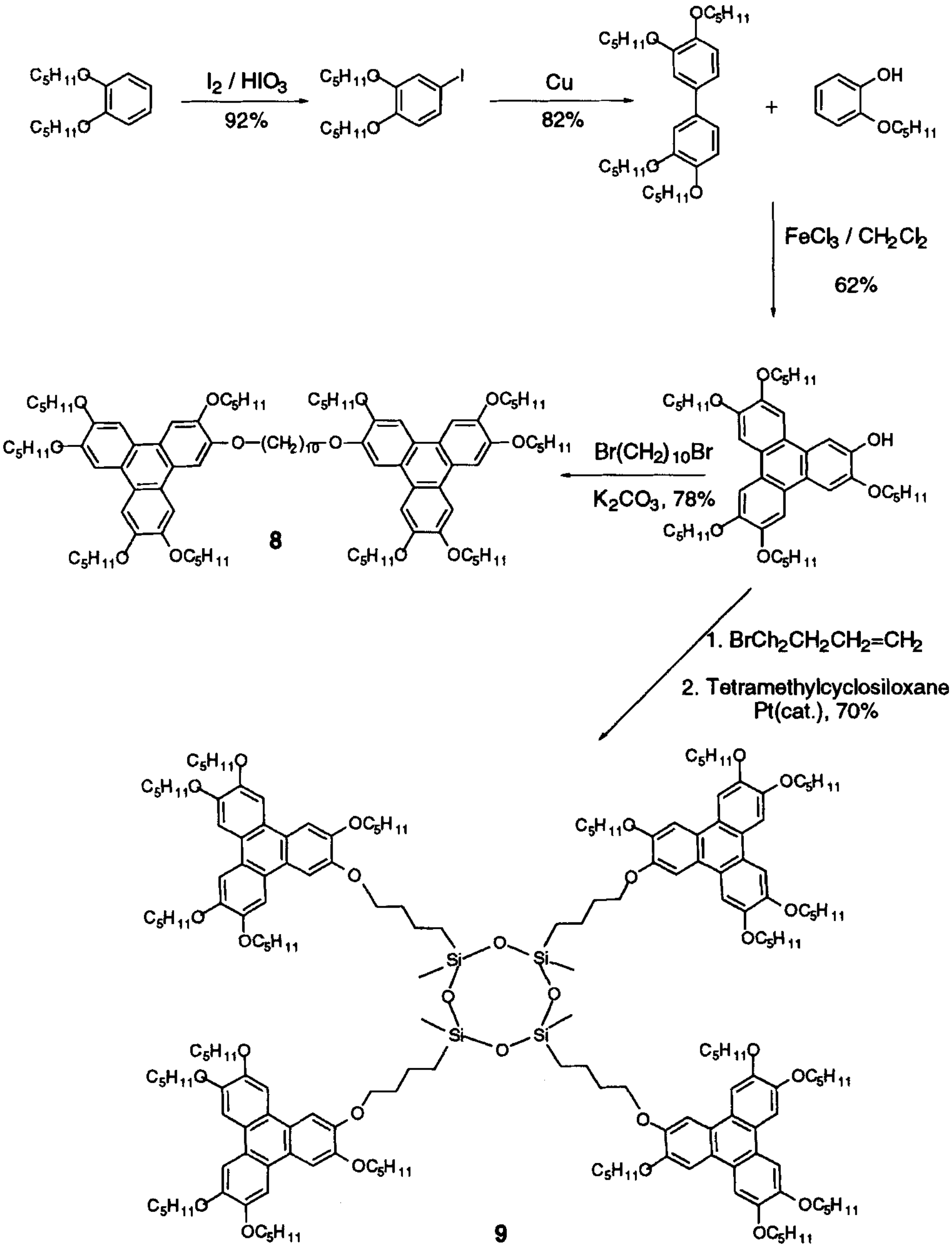
Hexasubstituted triphenylene derivatives are the most widely synthesized discotic liquid crystals. Symmetrically substituted hexaalkoxytriphenylenes can be prepared by oxidative trimerization of o-dialkoxybenzenes either with chloranil[17] or iron (III) chloride.[18-20] However, this approach to synthesize unsymmetrical triphenylene derivatives resulted in only very poor yields and envolves tedious separation of products. The so-called 'biphenyl route' has recently been developed[21,22] to synthesize these nonsymmetrical triphenylenes. But the classical trimerization of dialkoxybenzene and the biphenyl route can only be achieved with highly activated (electron rich) precursors and yields only hexa-substituted derivatives; cores with a low degree of substitution (*e.g.*, trialkoxytriphenylene) cannot be synthesized by these methods. Thus, triphenylenes having less than six alkoxy groups would be valuable intermediates for linkage of new substituents. To date, such derivatives can only be prepared efficiently by the effective yet complicated "terphenyl route".[23]

Previously, we have shown that all possible isomers of hexasubstituted mono, di, and trihydroxyalkoxytriphenylenes (**1-7**) are accessible by simple strategies, often in large scale. [24] The mono-functionalized triphenylenes, a valuable precursors for oligomers and polymers, can be synthesized directly by coupling tetraalkoxybiphenyl and alkoxyphenol using iron (III) chloride as oxidant in dry methylene chloride having catalytic amount of H_2SO_4 (Scheme 1). In order to simplify the following discussion the pentyloxy group will not be taken in account as functional groups. Thus, for example, compound monohydroxy pentapentyloxytriphenylene (**1**) will be written as monohydroxytriphenylene.



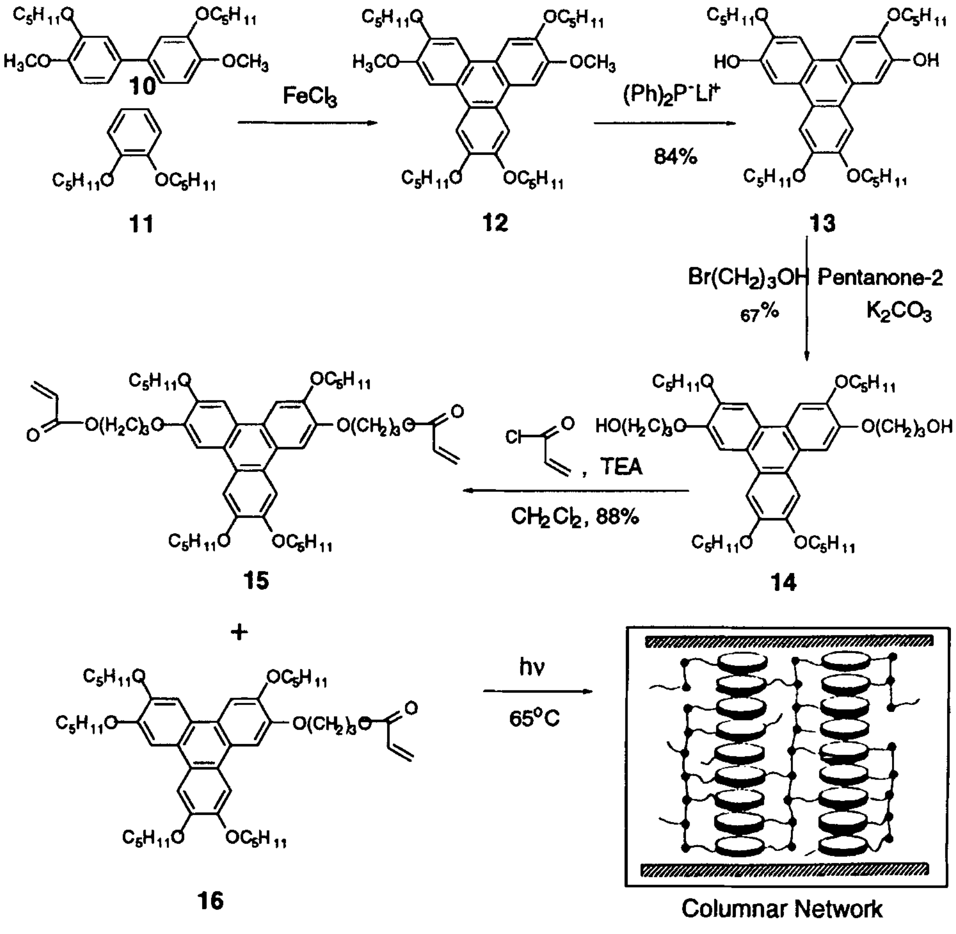
The monohydroxytriphenylene **1** was easily converted to a glassy dimer (**8**).[12,25] Such dimers in particular or discotic oligomers in general represent ideal model compounds for discotic polymers or networks due to their ease of purification, simple tailoring of the range of the mesophase by just varying the spacer length and the possibility to freeze in their columnar phase in a glassy state. Discotic twins based on benzene core was first reported by Lillya.[26] Praefcke and co-workers also found a biaxial nematic phase in the discotic twin formed by alkynylarene ethers.[27] The twin compound **8** with decyl spacer shows a glass transition around -59°C and a clearing point at 135°C. The photoconducting behavior of this dimer is very much similar to that of its monomer.[12] But if left at room temperature the compound slowly starts crystallizing. On heating the crystal melts at 64°C. Thus, a complete phase sequence of the dimer **8** is Cr 64°C (G -59°C) D_h 135°C i.

A stable glassy discotic is the tetramer of triphenylene **9** which was synthesized by first alkylating the monohydroxytriphenylene **1** with alkyl bromide having terminal olefin and the resulting product was reacted with commercially available tetramethylcyclosiloxane using Pt catalyst[28] (Scheme 1). The tetramer **9** is a room temperature discotic liquid crystal having glass transition temperature at -48°C and clearing point 141°C. It does not show any sign of crystallization on keeping for a long time at room temperature. The photoconducting behavior of this tetramer is similar to the triphenylene dimer (**8**).[29]



SCHEME 1 Synthesis of Monofunctionalized Triphenylene Derivatives

Difunctionalized triphenylenes (**2-5**) which are very valuable precursor molecules for the preparation of networks and main chain polymers, were synthesized as reported earlier,[24] by using the biphenyl route and a selective ether cleavage. For instance, synthesis of 2,7-dihydroxytetrapentyloxytriphenylene **13** was achieved (Scheme 2) by coupling dimethoxydipentyloxy biphenyl **10** with 1,2-dipentyloxybenzene **11** to yield dimethoxytetrapentyloxytriphenylene **12**. Two methoxy group of **12** were selectively cleaved by diphenylphosphide lithium[30] to dihydroxytriphenylene **13** possessing two reactive sites for further derivatization. Thus, alkylation of **13** with bromopropanol gives the dialcohol **14** which was converted to diacrylates **15** with acrylyl chloride in triethylamine.[24] This diacrylate does not show any mesomorphic behavior and is a crystalline solid with a melting point at 94°C.



SCHEME 2 Synthesis of Difunctionalized Triphenylene Derivatives

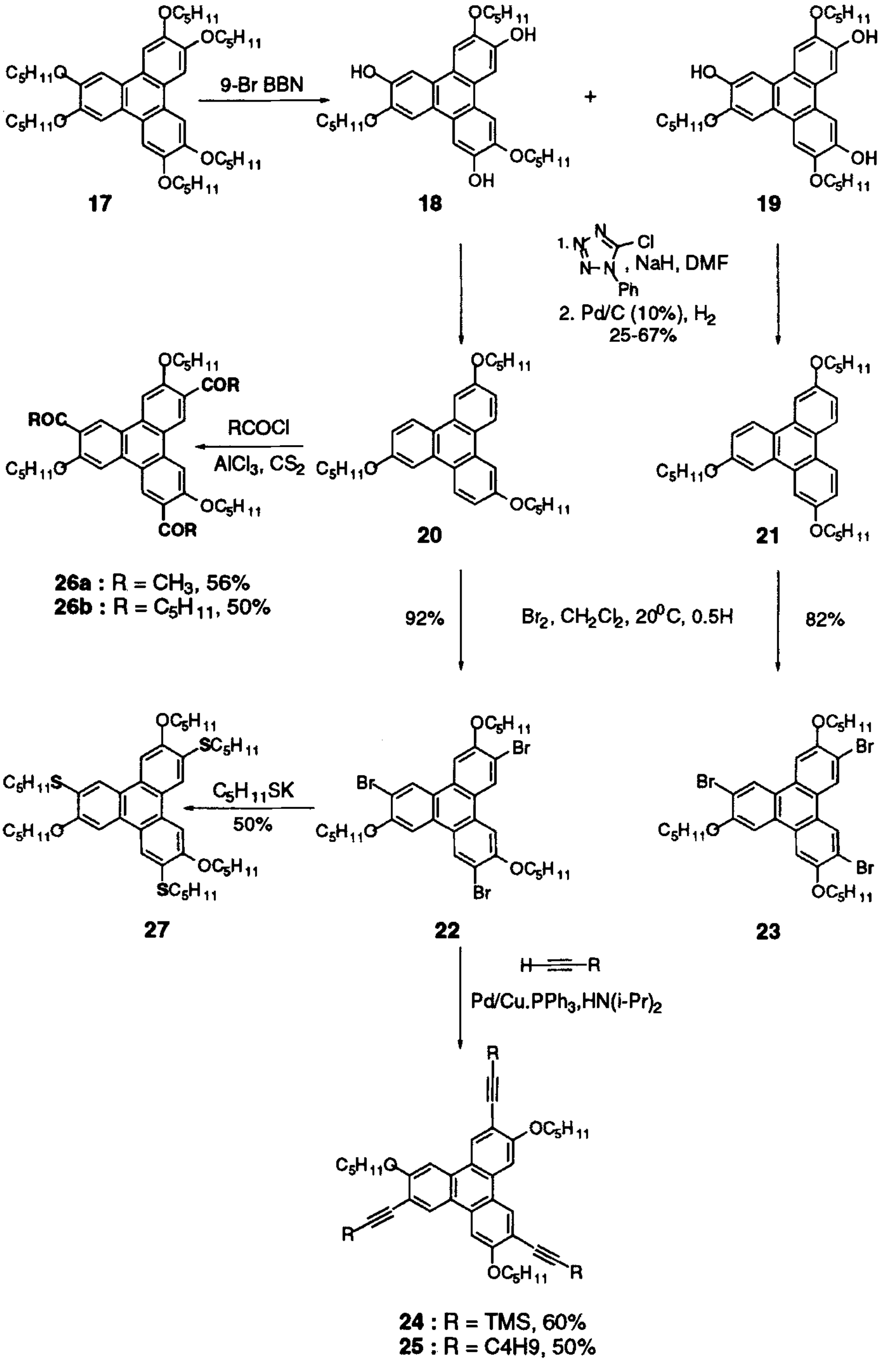
However a 1:1 mixture of the diacrylate **15** and monoacrylate **16**, prepared in the same manner from monohydroxytriphenylene, shows the hexagonal columnar phase with phase sequence Cr 59°C D_h 83°C i. A photopolymerization of this mixture at 65°C using 1% photoinitiator 2,2-dimethoxy-2-phenylacetophenone gives a columnar network which does not clear upto 300°C (Scheme 2). Further characterization of this material is in progress.

SYNTHESIS OF MIXED TAIL TRIPHENYLENE DISCOTICS

D. Adam et. al. recently reported a very high charge carrier mobility in the helical phase of HHTP[13]. This helical phase, having a long range intercolumnar order, has only been identified in HHTP and there are no other known examples of this phase in discotic liquid crystals. To understand the origin of this helical phase at the molecular level, we have recently initiated a research program focusing on the synthesis of low symmetry triphenylene derivatives having varying number of different chains and substituents attached to the core. We were particularly interested in the synthesis of a triphenylene derivative containing alternating alkoxy and alkylthio tails (**27**) attached to the same core, with the idea that the greater steric bulk of the S atoms alternated with smaller O atoms could induce helicity in the columnar packing of the mesophase of this molecule.

Synthesis of **27** and other mixed tail triphenylenes (**24-26**)[31] is outlined in Scheme 3. A selective cleavage[24] of only three alkoxy chains of HPT (**17**) yielded trialkoxytrihydroxytriphenylene derivatives **18** and **19**. The symmetrical and nonsymmetrical trialkoxytrihydroxytriphenylenes **18** and **19** were reduced to trialkoxytriphenylenes **20** and **21** by activating the phenols with a tetrazole unit followed by catalytic hydrogenation.[32] These reduced arenes **20** and **21** now possess reactive sites capable of derivatization via classical aromatic chemistry. Bromination of **20** and **21** with Br_2 in methylene chloride affords the tribromotriphenylenes **22** and **23**. To our surprise, both symmetrical and nonsymmetrical tribromotriphenylenes **22** (Cr 189°C D_h 217°C i) and **23** (Cr 112°C D_h 198°C i) are mesogenic and represent the best examples of triphenylene discotics having only three alkoxy chains in the periphery. It is interesting to note that none of the precursor trialkoxy molecules - trihdroxy (**18,19**), trireduced (**20,21**), or trimethoxy (not shown here) - are mesogenic. Clearly, the bulk of the bromine atom induces mesogenicity in these molecules. An effort to understand the effect of the size of halogen atoms attached directly to the core is now underway.

Synthesis of the desired tripentyloxytripentylthiotriphenylene **27** has been achieved in moderate yield (50%) by the Pd(0) catalyzed thiolation[33] of tribromo



SCHEME 3 Synthesis of Mixed Tail Triphenylene Derivatives

triphenylene **22** with the potassium salt of pentanethiol in NMP followed by quenching with pentylbromide. Efforts have not yet been made to optimize the yield.

Palladium/Cu catalyzed alkynylation[34] of **22** is highly efficient and gave different trialkynyltriphenylenes **24** (D_x 215°C D_h241°C i), **25** (D_{x1} 24°C D_{x2} 36°C D_h 171°C i) in high yields (Scheme 3).

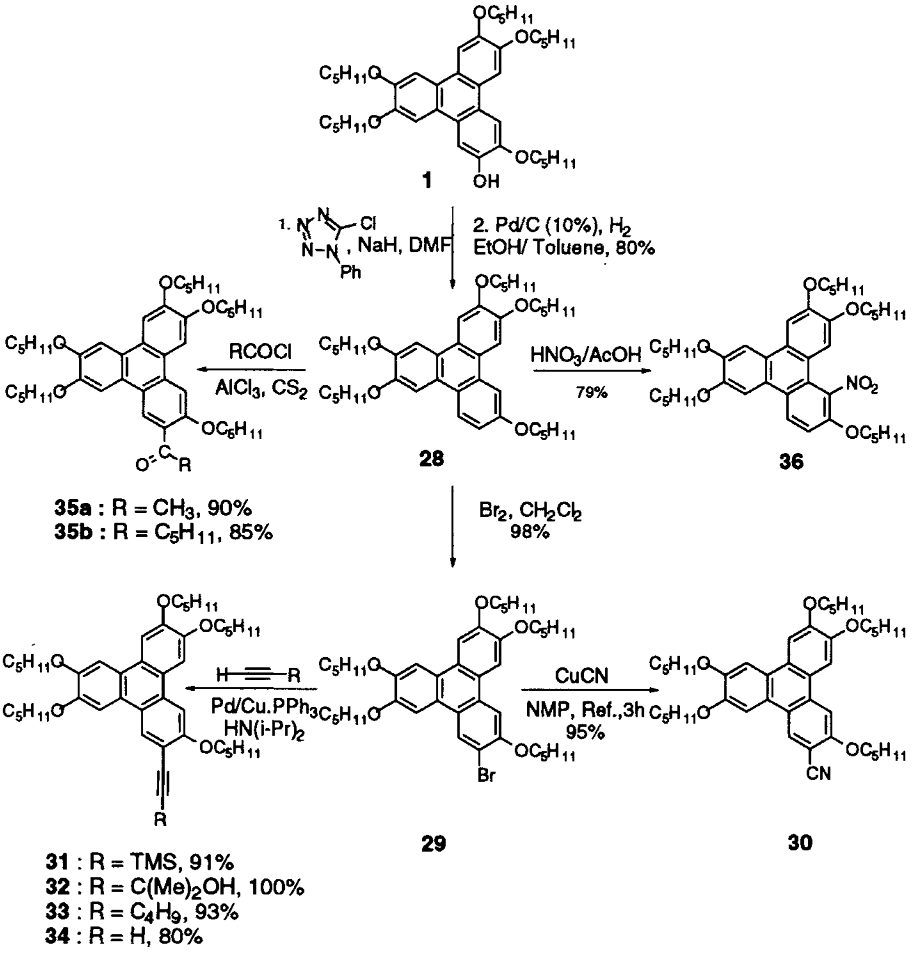
Friedel-Craft acylation of **20** with acyl chloride and hexanoyl chloride under classical reaction conditions gave triacyl **26a** (D_x 198°C D_h 253°C i) and trihexanoyltriphenylene **26b** (D_h 276°C i) in moderate yields (56% and 50% respectively). We have not yet successfully synthesized the nonsymmetric versions of these molecules. Electronic effects appear to favor electrophilic aromatic substitution of the symmetric trireduced triphenylene **20** over the non symmetric **21**.

SYNTHESIS OF FLUORESCENT TRIPHENYLENE DERIVATIVES

Most of the triphenylene derivatives so far known has a poor fluorescence efficiency[3,35] probably because of the high symmetry of the molecules. Boden et. al. recently reported the synthesis of colored triphenylene derivatives by nitrating triphenylene discotics at α position.[36] To study one-dimensional energy migration in the columnar phase[3] and LED behavior[8,16], we were interested to have highly fluorescent triphenylene discotic liquid crystals. In an effort to enhance fluorescence as well as the mesogenity of triphenylene discotic LCs, we have synthesized a number of new monofunctionalized triphenylene discotics bearing conjugative electron withdrawing substituents attached directly to the triphenylene core. Our strategy for optimization is two- fold. First, by extending the conjugation of the polyaromatic core of the LC, the maximum absorption (λ_{max}) should be red shifted and the fluorescence emission efficiency greatly enhanced.[35] Secondly, we hoped that the relatively low symmetry of monofunctionalized triphenylene discotics would result in a suppression of the melting point and thus, a broadening of the mesophase range. Steric asymmetry in the core can disfavor optimal packing of the cores thus inhibiting crystallization. Spiess and co-worker have demonstrated this general concept with a number of monoesterpentaalkoxy triphenylene discotics that are room temperature LCs with very low temperature glass transitions.[37] However, simple esterification would not allow us to significantly alter the electronic nature of the core. Thus, direct substitution at the triphenylene core was essential.

Scheme 4 summarizes the synthesis of monofuntionalized triphenylene derivatives.[38] The monohydroxytriphenylene (**1**) was reduced to arene **28** (m.p. 86°C) as mentioned above for the trihydroxytriphenylenes . The arene **28** on bromination with

Br_2 in methylene chloride gives the monobromo derivative **29** (D_x 14°C D_h 163°C i). Copper- mediated carbon-carbon bond formation with monobromo compound **29** is extremely efficient. Reaction of **29** with copper cyanide[39] in NMP gives the cyanotriphenylene **30** (Cr 51°C D_x 85°C D_h 226°C i) in 90% yield. Palladium/copper



SCHEME 4 Synthesis of Flurescent Triphenylene Derivatives

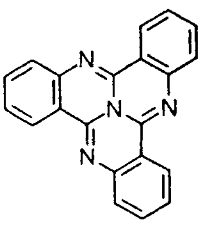
catalyzed alkynylation[34] of **29** can be accomplished in excellent yields with a variety of substituted alkynes as demonstrated with compounds **31** (D_h 184°C i), **32** (Cr 58°C D_h 180°C i) and **33** (D_x 16°C D_h 155°C i). Moreover, triphenylenes **31** and **32** can be deprotected to yield free phenylacetylenes for further elaboration or potential polymerization. For example, treatment of **32** with catalytic base gives alkyne **34** (D_h 146°C i[d]) in good yield.

Friedel-Crafts acylation of **28** with acetyl chloride and hexanoyl chloride in presence of aluminium trichloride proceeds in high yield with acylation occuring in the 3-position **35a** (Cr_1 58°C Cr_2 76°C D_h 169°C i), **35b** (Cr 63°C D_x 70°C D_h 184°C i). Surprisingly, classical nitration of **28** with nitric acid in acetic acid occurs preferentially in the sterically hindered 1 position **36** (m.p. 83°C) as unambiguously indicated in the ^{1}H NMR. This result contradicts claims that steric crowding strongly disfavors substitution in the 1-position relative to 2-and 3-positions.[36] Clearly, electronic effects dominate in the nitration of alkoxytriphenylenes.

All new meosogenic triphenylene derivatives show a depression in the melting point and a substantial broadening of the LC phase relative to the parent compound **17**. Phase sequence of all the derivatives are given in parenthesis after the structures. Assignment of a D_h phase in all the above triphenylene derivatives was determined by polarized optical microscopy. Focal conic textures very similar to that of compound 17[40] were observed for all of the new mesogenic derivatives. Qualitatively, all these monosubstituted triphenylene derivatives **30-35** are highly fluorescent[38] and quantitative determination of the fluorescence efficiency is now under investigation.

OTHER PHOTOCONDUCTING DISCOTICS

Photoconductivity in the columnar phases is also exhibited by other polyaromatic cores. several derivatives of tricycloquinazoline (**37**)[41,42] dibenzopyrene (**38**)[22] and phthalocyanine (**39**)[43] were synthesized as reported earlier. Full characterization of the new discotics and charge carrier mobility data will be published in due course.



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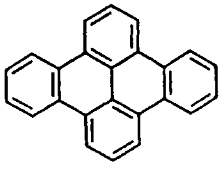

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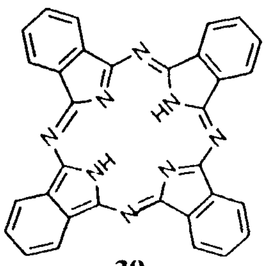

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CONCLUSIONS

Powerful synthetic methods are now available to prepare different functionalized triphenylene derivatives, oligomers, networks, mixed tail triphenylenes and fluorescent triphenylene discotic liquid crystals. Both electronic and physical properties of discotic liquid crystals can be tailored by these new synthetic methods. The columnar phase of these materials is highly suitable for fast charge carrier mobility. Photoconductivity in columnar phases is also exhibited by other polyaromatic cores such as tricycloquinazoline, dibenzopyrene and phthalocyanine.

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