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A convenient and economic method for the synthesis of monohydroxy-pentaalkoxy- and hexaalkoxytriphenylene discotics

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Abstract—A one-step process for the preparation of mono-functionalized triphenylene discotics is presented. Oxidative trimerization of *ortho*-dialkoxybenzenes using $FeCl_3$ in nitromethane and a catalytic amount of various acids, furnished monohydroxy-pentaalkoxytriphenylene in addition to hexaalkoxytriphenylene. These products can be easily separated by column chromatography over aluminium oxide.

Triphenylene derivatives are the most widely synthesized and well-characterized materials in the family of discotic liquid crystals (DLCs). Triphenylene as a novel core for DLCs was recognized in 1978 and since then more than 500 discotic liquid crystals based on a triphenylene core have been prepared.[1,2] These materials have been extensively studied for various physical properties such as one-dimensional charge and energy migration, electroluminescence, ferroelectric switching, alignment and self-assembling behaviour on surfaces and other properties.[3]

Hexamethoxytriphenylene (HMTP) was first prepared by the oxidative trimerization of 1,2-dimethoxybenzene (veratrol) in H_2SO_4 using chloranil or iron(III) chloride as oxidant.[4] The reaction represents an unusual case of the Scholl reaction where more than one aryl–aryl bond is formed.[5] Long alkoxy chain-substituted triphenylene derivatives, necessary to show mesomorphism, were prepared traditionally by demethylating HMTP and then realkylating the resultant hexaphenol with an appropriate alkyl halide. Later, the Boden group reported a direct synthesis of long alkyl chain-substituted hexaalkoxytriphenylene DLCs using only a catalytic amount of H_2SO_4 and iron(III) chloride as oxidant in a much improved yield.[6] We have recently reported a highly improved synthesis of triphenylene discotics using a novel reagent, $MoCl_5$.[7]

All these three reagents, chloranil, iron(III) chloride and molybdenum(V) chloride, are insoluble in common organic solvents and, therefore, addition of these materials, particularly on a large scale, is inconvenient. To overcome this problem, we have discovered a liquid oxidizing reagent, $VOCl_3$ for performing the oxidative trimerization.[8] Because of its miscibility in the solvent, it brings about almost spontaneous trimerization of *ortho*-dialkoxybenzenes into 2,3,6,7,10,11-hexaalkoxytriphenylenes. Though it allows milder reaction conditions, fewer purification problems and affords a better yield, it is expensive and moisture sensitive compared to $FeCl_3$. Therefore, we have examined the possibility of using $FeCl_3$ dissolved in nitromethane for this oxidative trimerization reaction. It has been reported that the trimerization reaction works only in dichloromethane, a hazardous chlorinated solvent,[8] so replacing it with nitromethane would have an additional advantage.

A small amount of monohydroxy-pentaalkoxytriphenylene (3,6,7,10,11-pentaalkoxy-2-triphenylenol) often forms in these reactions due to aryl-ether cleavage,[9] but its isolation is usually difficult. The mono-functionalized triphenylenes are highly valuable precursors for the synthesis of dimers, oligomers, side-chain polymers and networks. The physical properties of these non-conventional liquid crystals are significantly different

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Keywords: Triphenylene; Discotic liquid crystals; Monohydroxy-pentaalkoxytriphenylene; Oxidative trimerization; Iron(III) chloride.

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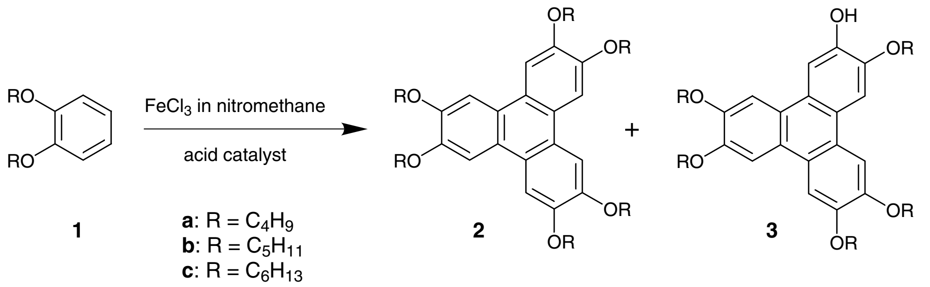
to those of conventional low molar mass liquid crystals. However, because of synthetic problems in obtaining the mono-functionalized triphenylenes, the potential utility of their discotic dimers, oligomers and polymers has not yet been fully explored. Recently, a few methods have been developed for the synthesis of mono-functionalized triphenylenes,[2] but these all involve multi-step synthesis. In this communication we report a one-step method for the preparation of a mixture of hexaalkoxytriphenylene and monohydroxy-pentaalkoxytriphenylene and a convenient process for the isolation of the latter.

The one-step synthesis of hexaalkoxytriphenylenes and monohydroxy-pentaalkoxytriphenylenes is shown in Scheme 1. In a typical reaction, the *ortho*-dialkoxybenzene **1** (1 mmol) was taken in nitromethane (5 mL) with the appropriate amount of acid catalyst.[10] To this was added a solution of $FeCl_3$ (3 mmol) in nitromethane (4 mL) and the reaction mixture was stirred at room temperature for 30 min under anhydrous conditions. It was then poured into cold methanol and the resultant precipitate was filtered off. The crude product was purified by column chromatography over neutral aluminium oxide. Elution of the column with 2–5% ethyl acetate in petroleum ether afforded the hexaalkoxytriphenylene **2** while elution with 10% ethyl acetate in petroleum ether furnished the pure monohydroxy-pentaalkoxytriphenylene **3**. The products were characterized from their spectral data, phase behaviour and by direct comparison with authentic samples. The amount of various acids used and yields of products are given in Table 1.

As can be seen from the Table 1, the best yields of 2,3,6,7,10,11-hexakis(butyloxy)triphenylene **2a**, 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene **2b** and 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene **2c** as well as of 3,6,7,10,11-pentakis(butyloxy)-2-triphenylenol **3a**, 3,6,7,10,11-pentakis(pentyloxy)-2-triphenylenol **3b** and 3,6,7,10,11-pentakis(hexyloxy)-2-triphenylenol **3c** were realized using 0.3% trifluoroacetic acid (TFA) in nitromethane. The most commonly used acid, sulfuric acid furnished smaller amounts of both products. While almost the same amount of hexaalkoxytriphenylenes **2** were obtained using HCl, a lower yield of the mono-functionalized triphenylenes **3** was obtained with this acid. Increasing the amount of acid, lowers the yield of both the products. Reactions conducted in the absence of acid gave lower yields (about 35%) of hexaalkoxytriphenylenes **2** and only traces of monohydroxytriphenylenes **3**. Longer chains prevent aryl-ether cleavage and thus, trimerization of longer chain substituted *ortho*-dialkoxybenzenes **1b** and **1c** results in lower yields of monohydroxy-pentaalkoxytriphenylenes **3b** and **3c**.

In conclusion, 15–20% yields of the valuable mono-functionalized triphenylenes **3a–c** can be isolated as by-products of the one-step oxidative trimerization of *ortho*-dialkoxybenzenes. The main product, hexaalkoxytriphenylenes, can be further converted into various functionalized triphenylenes using our previously reported method.[9b] The process reported here is a convenient, economic and high yielding method for the synthesis of these materials.



Scheme 1. Synthesis of hexaalkoxy- and monohydroxy-pentaalkoxytriphenylenes.

Table 1. Preparation of triphenylene derivatives using $FeCl_3$ in CH_3NO_2 solution at rt

Starting material	Acid (%)	Product (yield %)	
1a, **1b**, **1c**	TFA (0.3)	**2a** (65), **2b** (45), **2c** (53)	**3a** (20), **3b** (17), **3c** (15)
1a, **1b**, **1c**	TFA (1.0)	**2a** (64), **2b** (40), **2c** (48)	**3a** (18), **3b** (12), **3c** (14)
1a, **1b**, **1c**	TFA (5.0)	**2a** (45), **2b** (39), **2c** (30)	**3a** (6), **3b** (9), **3c** (1)
1a, **1b**, **1c**	TFA (10.0)	**2a** (42), **2b** (8), **2c** (28)	**3a** (5), **3b** (6), **3c** (0.5)
1a, **1b**, **1c**	H_2SO_4 (0.3)	**2a** (58), **2b** (43), **2c** (50)	**3a** (19), **3b** (13), **3c** (12)
1a, **1b**, **1c**	H_2SO_4 (1.0)	**2a** (47), **2b** (40), **2c** (49)	**3a** (7), **3b** (10), **3c** (11)
1a, **1b**, **1c**	H_2SO_4 (5.0)	**2a** (40), **2b** (24), **2c** (36)	**3a** (5), **3b** (1), **3c** (9)
1a, **1b**, **1c**	H_2SO_4 (10.0)	**2a** (17), **2b** (13), **2c** (9)	**3a** (1), **3b** (0), **3c** (0.5)
1a, **1b**, **1c**	HCl (0.3)	**2a** (64), **2b** (36), **2c** (49)	**3a** (14), **3b** (10), **3c** (9)
1a, **1b**, **1c**	HCl (1.0)	**2a** (48), **2b** (35), **2c** (45)	**3a** (7), **3b** (8), **3c** (5)
1a, **1b**, **1c**	HCl (5.0)	**2a** (31), **2b** (33), **2c** (28)	**3a** (1), **3b** (1), **3c** (0)
1a, **1b**, **1c**	HCl (10.0)	**2a** (12), **2b** (25), **2c** (22)	**3a** (0), **3b** (0), **3c** (0)

Yield represents the isolated pure product after column chromatography over aluminium oxide.

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10. Stock solutions of acid-containing nitromethane were prepared by mixing appropriate amounts (by volume) of AR grade concentrated acids (TFA, H_2SO_4, HCl) in nitromethane.