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Synthesis of monohydroxy-functionalized triphenylene discotics: green chemistry approach

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Abstract—This paper presents an environmentally benign procedure for the preparation of monohydroxy-functionalized triphenylenes using simple ionic reagents. Pyridinium hydrochloride, pyridinium hydrobromide, *N*-methyl pyridinium iodide, *N*-ethyl pyridinium bromide, and 1-*n*-butyl-3-methyl imidazolium bromide have been employed to prepare various monohydroxypentaalkoxytriphenylenes, which are valuable precursors for the synthesis of a variety of discotic monomers, dimers, oligomers, and polymers.
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1. Introduction

There has been an ever increasing interest in the field of discotic liquid crystals (DLCs) in general,[1] and in triphenylene-based discotic mesogens in particular,[2,3] since their discovery.[4,5] DLCs are a unique state of matter possessing self-organization of disk-shaped molecules. Their supramolecular columnar architecture is of fundamental importance, not only as models for the study of the energy and charge migration in organized systems, but also as functional materials for device applications such as one-dimensional conductors, photoconductors, light-emitting diodes, photovoltaic solar cells, gas sensors, etc. Triphenylene derivatives are the most widely synthesized and well-studied materials in the family of DLCs,[2,3] because they show a variety of mesophases, their derivatives are chemically and thermally stable, and their chemistry is fairly accessible. Scaled up and improved synthetic routes to the hexa-substituted triphenylene nucleus has been well documented.[6–9] However, because of synthetic problems in obtaining mono-functionalized triphenylenes, which are valuable precursor molecules for the synthesis of a variety of discotic dimers, oligomers, polymers, networks, and mixed tail derivatives, the potential utility of these intriguing materials has not yet been fully explored. Physical properties of these non-conventional liquid crystals are significantly different to those of conventional low molar mass liquid crystals. A few methods have been developed for the synthesis of mono-functionalized triphenylenes, but most of these involve expensive and hazardous reagents.

The synthesis of mono-functionalized triphenylenes can be achieved in different ways. One of the earliest reported methods[10] of monohydroxypentaalkoxytriphenylene synthesis involves partial alkylation of hexaacetoxytriphenylene to monoacetyl-pentaalkoxytriphenylene in low yield. This can be hydrolyzed to monohydroxytriphenylene. A non-selective cleavage of one of the alkoxy group of hexaalkoxytriphenylene using a calculated amount of 9-Br-BBN[11] gives a mixture of products containing unreacted hexaalkoxytriphenylene (26%), monohydroxytriphenylene (39%), and a minor amount of dihydroxytriphenylenes (10%). The desired product can be purified by column chromatography. A selective cleavage of the methyl ether of monomethoxypentaalkoxytriphenylene with lithium diphenylphosphide affords the monohydroxytriphenylene in high yield.[12,13] The monomethoxytriphenylene can be prepared by the so-called biphenyl route. The main drawback of this process is the poor yield of the biphenyl in the classical Ullman coupling reaction, and the use of highly sensitive and hazardous lithium diphenylphosphide. However, now better but expensive methods are available to prepare tetraalkoxybiphenyls.[14] Bushby and Lu have demonstrated the use of the isopropoxy masking group in a biphenyl–phenyl oxidative coupling route for the preparation of monohydroxytriphenylenes.[15] The synthesis of monohydroxytriphenylene by directly coupling tetraalkoxybiphenyl and alkoxyphenol using molybdenum(V) chloride has been reported,[9] but the reaction was sluggish and the isolation of the product was difficult. We have previously reported that this compound can also be obtained as a side product in the oxidative trimerization of dialkoxybenzene with $MoCl_5$ in about 25% yield.[9] Bromocatecholborane, an alternative to 9-Br-BBN, has been found to give almost 70% of mono-functionalized triphenylene.[16] This reaction is highly efficient for the preparation of mono-, di- and trifunctionalized triphenylene derivatives, but

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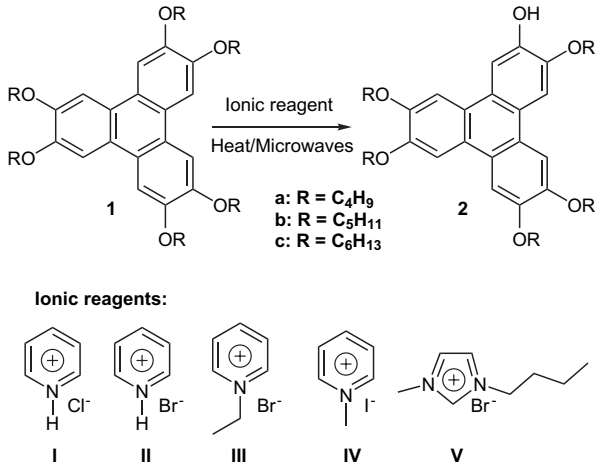
the reagent is expensive and moisture sensitive. Recently we have also reported[17] an economic and convenient method for the preparation of monohydroxy-functionalized triphenylene using $FeCl_3$ in nitromethane. Though it is a one-step process, the overall yield in the reaction does not go above 20%. Because of these problems, we started looking for an alternative, inexpensive, and less hazardous method to produce these materials. We have found that ionic reagents can be used to prepare these various monohydroxy-functionalized triphenylenes in moderate yield. This methodology avoids all type of toxic, volatile, and hazardous reagents.

Developing green chemistry methodologies is one of the main themes of modern synthetic chemistry. In this context, the use of ionic liquids and microwaves are powerful tools. Ionic liquids, a class of organic salts with usually low melting points, have attracted considerable attention.[18] Due to their unique characteristics, such as non-volatility, thermal stability, non-flammability, very low vapor pressure, reusability, and diverse solvating ability, they can be used as environmentally benign solvent media to replace conventional volatile organic solvents in many chemical processes.[19] Ionic liquids serve the dual purpose of solvent as well as reagents in many reactions, and allow easy isolation of products. On the other hand, microwave-assisted high-speed chemical synthesis has attracted much attention in the past decade.[20] Almost all types of organic reactions have been performed using the efficiency of microwave flash heating. This is not only due to the fact that the reactions proceed significantly faster and more selective than under conventional thermal conditions, but also because of operational simplicity, high yield of products and cleaner reactions with easier work-up. We have recently utilized this technology to prepare some conventional calamitic liquid crystalline materials.[21] In this paper, we report a convenient, economic and environmentally benign green chemical method for the synthesis of monohydroxypentaalkoxytriphenylenes by using pyridinium and imidazolium-based ionic reagents under classical as well as microwave heating conditions.

We have applied several pyridinium and imidazolium salts to examine the possibility of selective ether dealkylation in hexaalkoxytriphenylenes (Scheme 1) and the results are presented in the following tables. Pyridinium hydrochloride and hydrobromide have been prepared by following a closely related method reported in the literature.[22] These have been known for a long time, and a number of papers on their properties, chemical reactions, and reactivity are available.[23] These simple ionic reagents are very useful to cleave one of the ether linkages to get mono-functionalized triphenylene derivatives and a convenient, economic, and environmentally benign green chemical process for the isolation of the latter.



Scheme 1. Synthesis of monohydroxypentaalkoxytriphenylenes using ionic reagents.

2. Results and discussion

When different hexaalkoxytriphenylenes [R=$-C_4H_9$ (H4TP), $-C_5H_{11}$ (H5TP), $-C_6H_{13}$ (H6TP)] were treated with various ionic reagents (**I**–**V**) (Scheme 1), mono-functionalized triphenylenes were formed in good yields. A summary of the best yields and conditions is given in Table 1. More descriptive data are given in supplementary tables.

First of all, we checked the classical dealkylation reagent, pyridinium hydrochloride, to prepare mono-functionalized triphenylene. The hexaalkoxytriphenylene and different equivalents (1.2–4) of pyridinium hydrochloride were checked at about 165 °C at different time intervals (Table S1, Supplementary data) and the product was isolated by conventional work-up and purification. The use of 1.2 equiv of pyridinium hydrochloride furnished almost 16% of the mono-functionalized triphenylene derivative within 3 h. It is interesting to note that no side product was formed in the reaction and the unreacted triphenylene can be isolated easily. Therefore, the yield of the product **2** based on consumed H4TP was excellent. Increasing the reaction time to 24 h (entry 4, Table S1) resulted in the isolation of about 35% of monohydroxytriphenylene. The best yield was obtained by running the reaction for 48 h. It gives 40% of the desired monohydroxytriphenylene derivative but the product was contaminated with about 2% of dihydroxytriphenylenes. Increasing the amount of the reagent and keeping the same reaction time decreases the mono-functionalized derivative and increases dihydroxy functionalized triphenylene derivatives (6–8%). The same reaction condition has been used to cleave other triphenylenes. It is clear from Table 1 that longer chain aryl–alkyl ether gives lower yield of the product. This could be because of the increased steric hindrance of longer alkyl chains.

Table 1. Preparation of monohydroxypentaalkoxytriphenylene **2** using reagents **I**–**V** at 165–170 °C

Entry	**1**	Reagent (equiv)	Time (h)	**2** (%)
1	H4TP	**I** (3.0)	48	40
2	H5TP	**I** (3.0)	48	37
3	H6TP	**I** (3.0)	48	34
4	H4TP	**II** (4.0)	24	40
5	H5TP	**II** (4.0)	24	33
6	H6TP	**II** (4.0)	24	29
7	H4TP	**III** (3.2)	30	31
8	H5TP	**III** (3.2)	30	28
9	H4TP	**IV** (4)	24	37
10	H5TP	**IV** (4)	24	36
11	H6TP	**IV** (4)	24	31
12	H4TP	**V** (4.2)	24	33
13	H5TP	**V** (4.2)	24	33
14	H6TP	**V** (4.2)	24	30

To check whether Br^- cleaves the ether bond in hexaalkoxytriphenylenes more effectively than Cl^- we made simple pyridinium bromide by reacting HBr gas with pyridine. The cleavage of hexaalkoxytriphenylene using this reagent was carried out as described above for pyridinium hydrochloride and the results are summarized in Table S2 (Supplementary data). It is clear from this table that under identical reaction conditions (1.2 equiv of the reagent, 3 h), the yield of mono-functionalized triphenylene derivative increases to 21% but the product was contaminated with some amount of dihydroxy derivative. Increasing the reaction time or increasing the amount of the reagent does not show any significant change. Using 4 equiv of the reagent for 24 h, 40% of the desired mono-functionalized triphenylene can be isolated in addition to 10% of the dihydroxy derivatives. This reflects the higher reactivity of Br^- compare to Cl^-.

Pyridinium derivatives where alkyl groups are directly attached to the nitrogen of the pyridinium moiety have been rarely used for ether dealkylation. We have prepared some pyridine derivatives containing Br^- and I^- having an ethyl and methyl group, respectively. These reagents were prepared following a closely related literature procedure.[22] Their properties have already been described in the literature.[24] These reagents were also used to cleave one of the ether linkages of hexaalkoxytriphenylene as described above for pyridinium hydrochloride. As expected, these reagents produce less amounts of mono-functionalized triphenylene, and surprisingly the latter one does not give any mono-functionalized triphenylene derivative using 3 equiv of the reagent over 3 h. Tables S3 and S4 summarize the results of mono-functionalized triphenylene synthesis using these reagents.

The imidazolium-based ionic liquid was prepared following the literature method,[25] and found to be effective to cleave the ether bond. The hexaalkoxytriphenylene and different equivalents of imidazolium bromide were heated at about 165 °C for different time intervals (Table S5), and the product was isolated by conventional work-up and purified through column chromatography using neutral alumina. The best yield of mono-functionalized triphenylene was 33% after 24 h with 11% of dihydroxy derivative. The amount of reagent, reaction time, and temperature are summarized in Table S5.

We have also applied all the reagents (**I**–**V**) to prepare mono-functionalized triphenylene derivative under microwave irradiation. While reagents **I**, **III**, and **IV** did not give any mono-functionalized triphenylene under microwave heating condition for more than 5–10 min, reagents **II** and **V** produced the desired product. A summary of the best yields and conditions is given in Table 2. More descriptive data are given in supplementary Tables S6 and S7.

Table 2. Preparation of monohydroxypentaalkoxytriphenylene **2** using reagents **II** and **V** under microwave heating

Entry	**1**	Reagent (equiv)	MW power (W)	Time (min)	**2** (%)
1	H4TP	**II** (3.0)	360	5	36
2	H5TP	**II** (3.0)	360	5	34
3	H6TP	**II** (3.0)	600	3	28
4	H4TP	**V** (3.0)	600	3	26
5	H5TP	**V** (3.0)	360	5	30
6	H6TP	**V** (3.0)	600	3	30

The dealkylation of hexaalkoxytriphenylenes was carried out using an unmodified household microwave oven (LG, MS-192 W). We examined the effect of microwave power and time on various hexaalkoxytriphenylenes as described in Tables S6 and S7. The hexaalkoxytriphenylene and the ionic reagent were thoroughly mixed and subjected to microwave irradiation for 1 min under the desired power. The vial was taken out and once again kept back for 1 min and this procedure was continued up to desired time. Then the vial was cooled to room temperature. The mixture was dissolved in dichloromethane and then passed through column to isolate the pure product.

As can be seen from Tables S6 and S7, irradiation of the reaction mixture at 360 W for 3 min using 3 equiv of the reagent generally furnished good yield of the product. Enhancing the microwave power to 600 W or 800 W did not increase the yield significantly. Compared to thermal heating, the yield of monohydroxytriphenylenes was low under microwave heating conditions but the reaction can be finished in a very short time.

3. Conclusion

In conclusion, 30–40% yields of the valuable mono-functionalized triphenylenes can be isolated using a simple ionic liquid in thermal as well as microwave flash heating conditions. The use of 3 equiv of pyridinium hydrochloride for 48 h gives the best yield of mono-functionalized triphenylene. Using microwave flash heating, these materials can be prepared in a few minutes in moderate yield. In all cases, no side reaction occurred and the unreacted starting material can be isolated easily, and can be recycled. The process reported here is an economic and green synthesis method for the preparation of monohydroxyhexaalkoxytriphenylene derivatives.

4. Experimental

4.1. General

Chemical and solvents were obtained locally from E. Merck and used as such without any purification. Column chromatographic separations were performed on neutral aluminum oxide. TLC was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F254). NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer. The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (DSC; Perkin–Elmer, Model Pyris 1D), which was operated at a scanning rate of 5 °C min^{-1} both on heating and cooling. The apparatus was calibrated using indium (156.6 °C) as a standard.

4.2. Synthesis of mono-functionalized triphenylenes under thermal conditions

In a typical reaction, the hexaalkoxytriphenylene **1** (H5TP, 500 mg, 0.675 mmol) was taken in a round-bottomed flask with appropriate equivalents of the ionic reagent. The mixture was heated at 165–170 °C under sealed conditions for

different periods of time as shown in Table 1. The crude product was purified by column chromatography over neutral aluminum oxide. Elution of column with 2–5% ethyl acetate in petroleum ether afforded the hexaalkoxytriphenylene **1**, while the elution with 10% ethyl acetate in petroleum ether furnished the pure monohydroxypentaalkoxytriphenylenes **2**.

4.3. Synthesis of mono-functionalized triphenylenes under microwave irradiation

H4TP (330 mg, 0.5 mmol) was taken in a glass vial, [bmin]Br (330 mg, 1.5 mmol) was added, and the mixture was thoroughly mixed and irradiated for 1 min under the desired microwave power. The vial was taken out and once again kept back for 1 min and this procedure was continued up to desired time. Then the vial was cooled to room temperature. The mixture was dissolved in dichloromethane and then passed through a column to isolate the pure product.

4.4. Characterization

The monohydroxypentaalkoxytriphenylene derivatives were characterized from their spectral data, phase behavior, and by direct comparison with authentic samples. Spectral data of all the mono-functionalized derivatives with different peripheral chain lengths were found to be in accordance with the literature data.[12,13,16,26] Selected data are as follows.

Compound **2a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.83 (m, 4H), 7.78 (s, 1H), 5.90 (br s, 1H), 4.24 (m, 10H), 1.94 (m, 10H), 1.58 (m, 10H), 1.04 (t, J=7.2 Hz, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 148.8, 145.9, 145.3, 124.0, 123.7, 123.3, 123.0, 107.3, 106.6, 104.4, 69.6, 69.3, 68.8, 31.5, 19.4, 14.0; IR (KBr, all the derivatives **2a**–**2c** showed similar spectra): ν_{max} 3545, 2953, 2928, 2858, 1616, 1518, 1437, 1389, 1352, 1261, 1171, 1074, 835 cm^{-1}; UV–vis data ($CHCl_3$, all the derivatives **2a**–**2c** show similar spectrum): λ_{max} 276.8, 303.2, 344.0 nm; DSC (peak temperature in °C and associated enthalpy changes J/g in parentheses, Cr=crystals, I=isotropic): Cr 112.0 (56) I; Elemental analysis: calculated for $C_{38}H_{52}O_6$: C 75.47, H 8.66%; found: C 75.18, H 9.10%.

Compound **2b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.83 (m, 4H), 7.78 (s, 1H), 5.90 (br s, 1H), 4.24 (m, 10H), 1.94 (m, 10H), 1.50 (m, 20H), 0.98 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 149.0, 148.8, 145.9, 145.3, 124.0, 123.7, 123.3, 123.0, 107.6, 107.3, 106.5, 104.3, 69.9, 69.6, 69.1, 29.2, 29.0, 28.4, 22.6, 14.1; DSC: Cr 64 (28), Cr 82 (27) I; Elemental analysis: calculated for $C_{43}H_{62}O_6$: C 76.52, H 9.26%; found: C 76.29, H 9.60%.

Compound **2c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.83 (m, 4H), 7.78 (s, 1H), 5.90 (br s, 1H), 4.29 (m, 10H), 1.94 (m, 10H), 1.57 (m, 10H), 1.40 (m, 20H), 0.93 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 148.8, 145.9, 145.3, 124.0, 123.7, 123.2, 123.0, 107.7, 107.5, 107.3, 106.5, 104.4, 69.9, 69.7, 69.2, 31.7, 29.4, 29.3, 25.8, 22.7, 14.1; DSC: Cr 65 (63) I; Elemental analysis: calculated for $C_{48}H_{72}O_6$: C 77.38, H 9.74%; found: C 77.31, H 9.98%.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.058.

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