Synthesis of Functionalized Triphenylenes by Selective Ether Cleavage with *B*-Bromocatecholborane

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Abstract: This paper presents an efficient synthetic procedure for the preparation of mono-, di- and trifunctionalized triphenylene derivatives starting from the readily available hexakis(pentyloxy)triphenylene by selective ether cleavages with *B*-bromocatecholborane (2-bromo-1,3,2-benzodioxaboroles). Functionalized triphenylene derivatives are the precursor molecules for the preparation of processible triphenylene discotic dimers, oligomers, polymers and networks.

Key words: functionalized triphenylene, hexakis(pentyloxy)triphenylene, selective ether cleavage, discotic liquid crystals

Since the discovery of discotic liquid crystals,[1] there has been an ever increasing interest in the synthesis of new monomeric and polymeric discotic liquid crystals.[2] Though any device made of discotic liquid crystal has yet to come, the potential applications of these material in optoelectronics have recently been the subject of many discussions.[2–4] In the columnar mesophase, molecules stack one on top of the other with a stacking distance of about 3–4 Å, making these molecules perfectly suitable for one-dimensional charge migration. Conductivity, photoconductivity and energy migration in the columnar phase of various discotic liquid crystals (LCs) have been studied extensively.[5–10]

Discotic LCs based on triphenylene core are the most widely synthesized and well-studied materials in the family of discotics. Due to their pronounced photoconductivity and high charge carrier mobility, triphenylene-based columnar discotic LCs show great potential as molecular organic materials for optoelectronic devices. Several research groups are currently working on the synthesis of symmetrical, unsymmetrical and functionalized triphenylene derivatives.[11–41] We have very recently reported a highly improved synthesis of symmetrical, unsymmetrical and monofunctionalized triphenylene derivatives using a novel reagent $MoCl_5$.[35] We have also reported earlier the synthesis of various functionalized triphenylene,[4, 29] mixed tail triphenylene,[33] low symmetry, fluorescent triphenylene[32] and core functionalized triphenylene discotic LCs.[36–38] Because of synthetic problems in obtaining the functionalized triphenylene derivatives in high yield, the potential utility of discotic dimers, oligomers and polymers has not yet been fully explored. In this communication, we wish to report a simple, easy and high overall yielding method for the preparation of mono-, di- and trifunctionalized triphenylene derivatives. In order to simplify the discussion hexakis(pentyloxy)triphenylene is written as H5TP, and monofunctionalized means monohydroxy-pentaalkoxytriphenylene. The pentyloxy groups are not considered as functional groups. Thus, for example, compound monohydroxy-pentakis(pentyloxy)triphenylene **2** is written as monohydroxy-H5TP or monofunctionalized-H5TP and compound trihydroxy-tris(pentyloxy)triphenylene **5** is written as trihydroxy-H5TP or trifunctionalized-H5TP.

The monofunctionalized triphenylenes are very valuable precursors for the synthesis of dimers, oligomers, side-chain polymers and networks. The synthesis of monofunctionalized triphenylenes **2** can be achieved by different ways. Hexakis(pentyloxy)triphenylene **1** can be prepared by oxidative trimerization of *o*-dialkoxybenzene with chloranil,[11] iron(III) chloride[19] or molybdenum(V) chloride.[35] A nonselective cleavage of one of the alkoxy chains of hexaalkoxytriphenylene can be done by the use of a calculated amount of 9-Br-BBN[30] which gives a mixture of products containing unreacted hexaalkoxytriphenylene (26%), monohydroxytriphenylene (39%) and minor amount of dihydroxytriphenylenes (10%). The desired product can be purified by column chromatography. Similarly, a nonselective synthesis can also be achieved[13] by the partial alkylation of hexaacetoxytriphenylene to monoacetyltriphenylene in low yield (26%) which can be hydrolyzed to monohydroxytriphenylene. A selective cleavage of the methyl ether of monomethoxypentaalkoxytriphenylene with lithium diphenylphosphide gives the monohydroxytriphenylene in high yields.[31] The monomethoxytriphenylene was 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. We have very recently reported the synthesis of monohydroxytriphenylene by directly coupling tetraalkoxybiphenyl and alkoxyphenol using molybdenum(V) chloride as oxidant in dichloromethane in moderate yield.[35] Though this represents one of the best method for the preparation of monohydroxytriphenylene, the moderate yield of the final oxidative coupling reaction and the Ullmann reaction for the preparation of the biphenyl results, overall, in a poor yield of the final product. We have also reported that this compound can also be obtained as a side product in the oxidative trimerization of dialkoxybenzene with $MoCl_5$ or $FeCl_3$ in about 25% yield.[35, 38]

The two hydroxy groups in a dihydroxytetraalkoxytriphenylene may be present in four different ways. These are at the 2,3-, 2,6-, 2,7-, and 3,6-positions.[28, 30] Synthesis of dihydroxytriphenylene was achieved by statistical methods. Alkylation of hexaacetoxytriphenylene with alkyl halide gives a mixture of dihydroxytriphenylene in 29% yield.[15] Difunctionalized triphenylene of well-de-

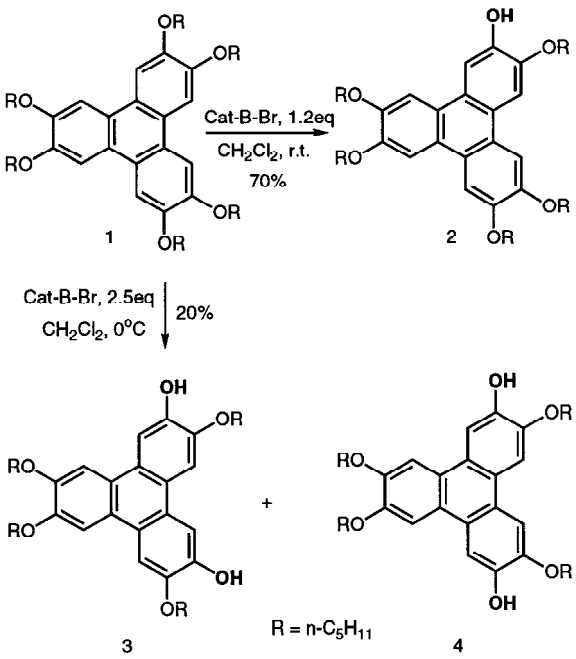
fined structure can be prepared by using the biphenyl route and a selective ether cleavage.[28, 30] The multiple step synthesis involves the preparation of different dimethoxy-tetraalkoxytriphenylene and finally the two methoxy groups were selectively cleaved by lithium diphenylphosphide to dihydroxytriphenylene.[28] This rational synthesis is extremely important for the preparation of authentic samples, but the generally poor yield obtained in the Ullman reaction, the use of highly sensitive, hazardous and costly lithium diphenylphosphide, and overall poor yield because of multiple steps (5–10% from catechol), make this method uneconomical on a large scale.

Trifunctionalized triphenylenes are particularly important for the preparation of "mixed tail" discotics, and as cross-linkers for the preparation of discotic networks and elastomers. Previously these compounds were prepared by the selective ether cleavage of hexaalkoxytriphenylene with bulky Lewis acid, 9-Br-BBN.[4, 30] Very recently, the same reagent has been used by Kilburn to prepare these trifunctionalized derivatives in a modified way.[41] Because of handling problem of this pyrophoric moisture-sensitive reagent, we started looking its alternative and have found that *B*-bromocatecholborane is superior to 9-Br-BBN.

The ability of *B*-bromocatecholborane (Cat-B-Br), also named as 2-bromo-1,3,2-benzodioxaboroles or catechol boron bromide, to cleave certain ether, ester and carbamate groups under mild conditions is known from the literature.[42, 43] We anticipated that this monofunctionalized, bulky Lewis acid will have better regioselectivity than commonly used boron tribromide and may cleave selectively one, two and three alkoxy chains of hexaalkoxytriphenylene. The reagent can be readily prepared by reacting catechol with boron tribromide. The colorless solid is stable for months, but can be stored more easily as CH_2Cl_2 solutions.[42, 43]

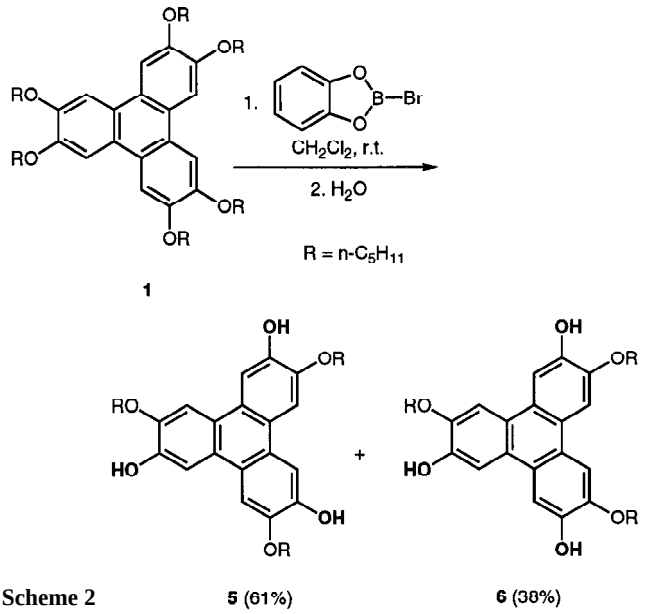
The cleavage of hexaalkoxytriphenylene with different concentration of Cat-B-Br is given in the Table. When H5TP **1** is treated with 1–1.2 equivalents of the reagent in dichloromethane at room temperature for 24–48 hours, it gives mainly the monohydroxy-H5TP **2** with a minor amount of unreacted H5TP **1** (Scheme 1). Increase in reaction time and temperature does not change the yield of monohydroxy-H5TP **2** significantly. An increase in the concentration of the reagent produces cleaving of the other alkoxy chains and variable amounts of mono-, di-, and trifunctionalized-H5TP are obtained (Table).

Reaction of H5TP with 2–2.4 equivalents of Cat-B-Br at room temperature to prepare difunctionalized-H5TP always gives a mixture of mono- **2**, di- **3** + **4**, and trifunctionalized-H5TP **5** and **6** (Table, entries 8 and 9). However, the formation of trihydroxytriphenylenes **5** and **6** can be checked by performing the reaction at 0 °C and the dihydroxy derivatives **3** + **4** can be isolated in reasonably good quantity (Scheme 1). Nevertheless, all the products can be easily separated by simple column chromatography over silica gel and as all the functionalized triphenylenes can be utilized to prepare a variety of other derivatives, nothing goes to waste. In all the cases almost quantitative material balance was observed. Out of the four possible isomers of dihydroxy-H5TP, we found that only 2,6- and 2,7-isomers, **3** and **4**, respectively, are the major products. These two **3** + **4** can be separated by a careful and repeated chromatography over basic alumina in about 6:4 ratio. We actually separated only a small amount of these isomers for physical and spectral characterization, in all other cases global yield of the two isomers is given in the Table. Trace (less than 1%) of the 3,6-isomer was also present in some cases but the 2,3-isomer, as expected because of the bulkiness of the reagent, was completely absent.



Scheme 1

The real advantage of this monofunctionalized, bulky Lewis acid was found in the preparation of trifunctional triphenylene. Treatment of H5TP **1** with 3.6 equivalents of Cat-B-Br in dichloromethane at room temperature for 36 hours gives exclusively two products, the symmetrical 2,6,10-trihydroxy-3,7,11-tris(pentyloxy)triphenylene **(5)** (61%) and nonsymmetrical 2,7,10-trihydroxy-3,6,11-tris(pentyloxy)triphenylene **(6)** (38%) (Scheme 2). Use of less than 3.6 equivalents of the reagent ca. 3.0 equivalents under similar conditions gives a small amount (6%) of dihydroxy-H5TP **3**/**4** in addition to the two trifunctionalized-H5TP **5** and **6**. Reducing the time to 24 hours with 3.6 equivalents of reagent also gives about 5% of dihydroxy-H5TP. Excess reagent, ca. 4 equivalents, gives more or less the same result obtained from the use of 3.6 equivalents of reagent (Table). The high selectivity of the *B*-bromocatecholborane could be due to the very bulkiness of the reagent that allows the cleavage of only one alkyl chain per ring. The two symmetrical and nonsymmetrical trifunctionalized triphenylenes can be separated very easily by simple column chromatography on silica gel.



Scheme 2

In summary, this work describes an efficient method for the preparation of monofunctionalized, difunctionalized and trifunctionalized triphenylenes starting from the easily available hexaalkoxytriphenylene. Functionalized triphenylenes are extremely important for the preparation of discotic dimers, oligomers, polymers, and networks. The use of this reagent can be extended to other polyaromatic systems, e.g., truxene, dibenzopyrene, decacyclene, etc., and this will open a route for the preparation of a variety of new mixed tail discotics.

Table. Cleavage of H5TP with Cat-B-Br (CH_2Cl_2, r.t.)

Entry	Reagent (Equiv.)	Time (h)	Products Yield (%)				
			1	**2**	**3+4**	**5**	**6**
1	1.0	24	39	60	–	–	–
2	1.0	36	34	65	–	–	–
3	1.2	24	32	66	–	–	–
4	1.2	36	32	67	–	–	–
5	1.2	48	28	70	–	–	–
6[a]	1.2	4	30	68	–	–	–
7	1.6	36	20	69	6	–	–
8	2.0	36	19	33	14	17	7
9	2.4	36	12	39	15	20	10
10[b]	2.2	48	31	35	10	–	–
11[b]	2.4	48	24	42	18	–	–
12[b]	2.5	48	22	40	20	–	–
13	3.0	48	–	–	6	56	36
14	3.6	24	–	–	5	55	37
15	3.6	36	–	–	–	61	38
16	4.0	36	–	–	–	60	38

[a] Reflux.
[b] 0°C.

Chemicals and solvents were obtained locally from E. Merck and used as such without any purification. Column chromatographic separations were performed on silica gel (Spectrochem, 230–400 mesh). TLC was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer. Mps were taken on a DSC 7 (Perkin–Elmer) with heating and cooling rate of 5°C per min and the onset reading is given. Mps of the crystals obtained from solvent (1st heating) differ from the mp of crystals obtained from melt (2nd heating) and, therefore, both are given. Compounds **2** and **3** show at least one broad solid–solid transition prior to the melting. H5TP was prepared as reported.[35]

***B*-Bromocatecholboronane:**[42, 43]
To a cooled solution (–15°C) of BBr_3 (18 g, 0.072 mol) in CH_2Cl_2 (10 mL) was added a suspension of catechol (7.1g, 0.065mol) in CH_2Cl_2 (50 mL) in portions with stirring under argon. The mixture was brought to r.t., the solvent removed and the product distilled under vacuum. The white solid was used to make a 0.5 M solution by mixing the product (11.0 g) with CH_2Cl_2 (100 mL) and this was used for different ether cleavage reactions.

Cleavage of Alkoxy Chains of H5TP with *B*-Bromocatecholborane: General Procedure:
A solution of H5TP **1** (200 mg, 0.27 mmol) was dissolved in anhyd CH_2Cl_2 (5 mL) and cooled to 0°C. To this was added the desired amount of *B*-bromocatecholborane solution in CH_2Cl_2 under argon and the mixture was stirred at r.t. for the specified time (Table). After that it was poured over ice-water and extracted with CH_2Cl_2, the combined extract was dried (anhyd Na_2SO_4), solvent was removed under vacuum and the crude product was purified by column chromatography (silica gel, hexane/CH_2Cl_2). The R_f value of the spots on TLC in two different solvent systems, A (hexane/CH_2Cl_2 2:8); B (hexane/EtOAc 8:2) is given.

Monohydroxy-H5TP **(2)**: mp 70.3°C (MeOH, 1st heating), 69.9°C (melt, 2nd heating), (Lit.[31] mp 70°C); R_f 0.73 (A); 0.63 (B).

2,6-Dihydroxy-H5TP **(3)**: mp 85.8°C (MeOH, 1st heating), 85.9°C (melt, 2nd heating), (Lit.[30] mp 82.5°C); R_f 0.66 (A); 0.46 (B).

2,7-Dihydroxy-H5TP **(4)**: mp 190.9°C (hexane/EtOAc, 1st heating), 186.2°C (melt, 2nd heating), (Lit.[30] mp 180°C); R_f 0.61 (A); 0.48 (B).

3,6-Dihydroxy-H5TP: mp 143.3°C (hexane/EtOAc, 1st heating), 142.1°C (melt, 2nd heating), (Lit.[30] mp 142.5°C); R_f 0.36 (A); 0.28 (B).

2,6,10-Trihydroxy-H5TP **(5)**: mp 162.3°C (EtOH, 1st heating), 140.9°C (melt, 2nd heating), (Lit.[30] mp 140°C, Lit.[41] mp 157.8°C); R_f 0.64 (A); 0.38 (B).

2,7,10-Trihydroxy-H5TP **(6)**: mp 149.1°C (EtOH, 1st heating), 148.5°C (melt, 2nd heating), (Lit.[30] mp 146°C, Lit.[41] mp 119–120°C); R_f 0.23 (A); 0.21 (B).

NMR data of all the derivatives were found to be in accordance with literature data.[30, 31]

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(1) Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana.* **1977**, 9, 471.
(2) For a brief review of discotics see Chandrasekhar, S. *Liq. Cryst.* **1993**, *14*, 3.
See also Chandrasekhar, S.; Kumar, S. *Sci. Spec.* **1997**, *8*, 66.
(3) Boden, N.; Bissell, R.; Clements, J.; Movaghar, B. *Liquid Crystals Today* **1996**, *6*, 1.
(4) Kumar, S.; Schuhmacher, P.; Henderson, P.; Rego, J.; Ringsdorf, H. *Mol. Cryst. Liq. Cryst.* **1996**, *288*, 211.
(5) Schouten, P. G.; Warman, J. M.; deHaas, M. P.; van Nostrum, C. F.; Gelinck, G. H.; Nolte, R. J. M.; Copyn, M. J.; Zwikker, J. W.; Engel, M. K.; Hanack, M.; Chang, Y. H.; Ford, W. T. *J. Am. Chem. Soc.* **1994**, 116, 6880 and references therein.

(6) Boden, N.; Borner, R. C.; Bushby, R. J.; Clements, J. *J. Am. Chem. Soc.* **1994**, *116*, 10807 and references therein.
(7) Arikainen, E. O.; Boden, N.; Bushby, R. J.; Clements, J.; Movaghar, B.; Wood, A. *J. Mater. Chem.* **1995**, *5*, 2161 and references therein.
(8) Simmerer, J.; Glusen, B.; Paulus, W.; Kettner, A.; Schuhmacher, P.; Adam, D.; Etzbach, K. H.; Siemensmeyer, K.; Wendorff, J. H.; Ringsdorf, H.; Haarer, D. *Adv. Mater.* (Weinheim, Ger.) **1996**, *8*, 815 and references therein.
(9) van de Craats, A. M.; Warman, J. M.; deHaas, M. P.; Adam, D.; Simmerer, J.; Haarer, D.; Schuhmacher, P. *Adv. Mater.* (Weinheim, Ger.) **1996**, *8*, 823 and references therein.
(10) Markovitsi, D.; Germain, A.; Millie, P.; Lecuyer, P.; Gallos, L. K.; Argyrakis, P.; Bengs, H.; Ringsdorf, H. *J. Phys. Chem.* **1995**, *99*, 1005 and references therein.
(11) Destrade, C.; Mondon, M. C.; Malthete, J. J. *Phys. Colloq. C3.* **1979**, *40*, 17.
(12) Tinh, N. H.; Bernaud, M. C.; Sigaud, G.; Destrade, C. *Mol. Cryst. Liq. Cryst.* **1981**, *65*, 307.
(13) Kreuder, W.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 807.
(14) Le Berre, V.; Simonet, J.; Batail, P. *J. Electroanal. Chem.* **1984**, *169*, 325.
(15) Kreuder, W.; Ringsdorf, H.; Tschirner, P. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 367.
(16) Bushby, R. J.; Hardy, C. *J. Chem. Soc., Perkin Trans. I* **1986**, 721.
(17) Le Berre, V.; Angely, L.; Simonet-Gueguen, N.; Simonet, J. *J. Chem. Soc., Chem. Commun.* **1987**, 984.
(18) Chapuzet, J.; Simonet, J. *Tetrahedron* **1991**, *47*, 791.
(19) Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851.
(20) Boden, N.; Bushby, R. J.; Cammidge, A. N. *J. Chem. Soc., Chem. Commun.* **1994**, 465.
(21) Borner, R. C.; Jackson, R. F. W. *J. Chem. Soc., Chem. Commun.* **1994**, 845.
(22) Goodby, J. W.; Hird, M.; Toyne, K. J., Watson, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1701.
(23) Naarmann, H.; Hanack, M.; Mattmer, R. *Synthesis* **1994**, 477.
(24) Boden, N.; Bushby, R. J.; Cammidge, A. N. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 307.
(25) Boden, N.; Bushby, R. J.; Cammidge, A. N. *Liq. Cryst.* **1995**, *18*, 673.
(26) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Headdock, G. *J. Mater. Chem.* **1995**, *5*, 2275.
(27) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Headdock, G. *Synthesis* **1995**, 31.
(28) Boden, N.; Bushby, R. J.; Cammidge, A. N. *J. Am. Chem. Soc*. **1995**, *117*, 924.
(29) Henderson, P.; Kumar, S.; Rego, J. A.; Ringsdorf, H.; Schuhmacher, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1059.
(30) Closs, F.; Häussling, L.; Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *J. Chem. Soc., Perkin Trans. I* **1995**, 829.
(31) Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *Liq. Cryst.* **1995**, *18*, 191.
(32) Rego, J. A.; Kumar, S.; Ringsdorf, H. *Chem. Mater.* **1996**, *8*, 1402.
(33) Rego, J. A.; Kumar, S.; Dmochowski, I. J.; Ringsdorf, H. *J. Chem. Sci., Chem. Commun.* **1996**, 1031.
(34) Kumar, S. *Mol. Cryst. Liq. Cryst.* **1996**, *289*, 247.
(35) Kumar, S.; Manickam, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1615.
(36) Kumar, S.; Manickam, M.; Chandrasekhar, S. *Indian Patent Appl. No*. 10329, 1997.
(37) Kumar, S.; Manickam, M. *Mol. Cryst. Liq. Cryst.* **1998**, *309*, 291.
(38) Kumar, S.; Manickam, M.; Balagurusamy, V. S. K.; Schonherr, H. (to be published).
(39) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Duckworth, S.; Headdoc, G. *J. Mater. Chem.* **1997**, *7*, 601.
(40) Praefcke, K.; Eckert, A.; Blunk, D. *Liq. Cryst*. **1997**, *22*, 113.
(41) Wright, P. T.; Gillies, I.; Kilburn, J. D. *Synthesis* **1997**, 1007.
(42) Boeckman, Jr., R. K.; Potenza, J. C. *Tetrahedron Lett.* **1985**, *26*, 1411.
(43) King, P. F., Stroud, S. G. *Tetrahedron Lett.* **1985**, *26*, 1415