Synthesis of Triphenylene and Dibenzopyrene Derivatives: Vanadium Oxytrichloride a Novel Reagent

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Abstract: This paper presents an efficient synthetic procedure for the preparation of various triphenylene and dibenzopyrene derivatives using $VOCl_3$ as a novel reagent. Symmetrically substituted hexaalkoxytriphenylenes are obtained from *o*-dialkoxybenzenes by oxidative trimerization with $VOCl_3$ in high yields. The oxidative coupling of a 3,3',4,4'-tetraalkoxybiphenyl and 1,2-dialkoxybenzenes or 1,2,3-trialkoxybenzenes affords unsymmetrically substituted derivatives of triphenylene. The reagent oxidizes 3,3',4,4'-tetraalkoxybiphenyl efficiently to 2,5,6,9,12,13-hexaalkoxydibenzo[*fg,op*]naphthacene-1,8-quinone and its 1,10-quinone isomer. Both the quinones can be converted to liquid crystalline derivatives using well-established chemistry. Effects of solvent, reagent concentration, acid catalyst and temperature have been studied.

Key words: triphenylene, dibenzopyrene, vanadium oxytrichloride, oxidative coupling, discotic liquid crystals

The supramolecular assemblies of disc-shaped molecules lead to the formation of discotic liquid crystals.[1] These materials are becoming of increasing interest as self-organizing molecular wires through which charge or excitons can migrate rapidly.[2] Charge mobility along the molecular columns was reported to be several orders of magnitude higher than that observed for the organic polymers.[3] Because of this property, their potential applications in conducting, photoconducting systems, optical data storage, light emitting diodes, photovoltaic solar cells, gas sensors, and other devices have been envisaged.[4-6]

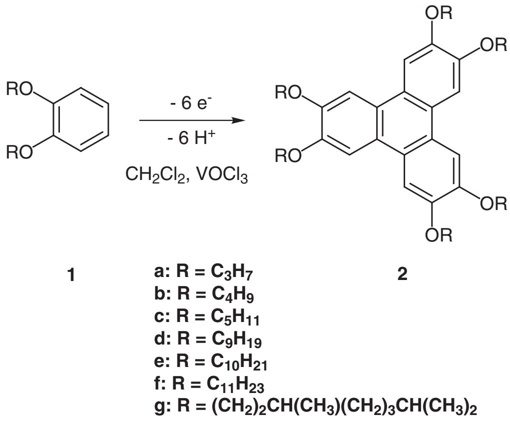
Triphenylene (TP) and dibenzopyrene (DBP; Chemical Abstract nomenclature for this molecule is dibenzo[*fg,op*]naphthacene) are two very important cores in the field of discotic liquid crystals. The formation of discotic liquid crystals by triphenylene molecule was reported[7] just after the discovery of discotic liquid crystals in 1977.[8] Since then triphenylene remains the focus of attention of liquid crystal scientists around the world and a variety of triphenylene derivatives have been synthesized and extensively studied for various physical properties.[6] The DBP core appeared in the LC field very recently[9] but has become the focus of attention because of the ferroelectric switching of columnar mesophases of these derivatives. In a preliminary communication, we have earlier reported the use of vanadium oxytrichloride for the oxidative trimerization of *o*-dialkoxybenzenes to hexaalkoxy-TP.[10] We have now discovered that vanadium oxytrichloride is also a novel reagent for the oxidative dimerization of tetraalkoxybiphenyl to dibenzopyrene derivatives. Here we report the preparation of several triphenylene and dibenzopyrene derivatives using $VOCl_3$ under various reaction conditions.

Synthesis of Hexaalkoxytriphenylenes

The formation of aryl-aryl bonds, particularly by oxidative coupling of phenols and phenol ethers is a key step in biological systems for the synthesis of various complex molecules. Both, intermolecular and intramolecular C-C bond formation between aromatic rings is effected under suitable oxidizing conditions and can be accomplished by chemical, electrochemical or photochemical means. When this chemical reaction is carried out under the influence of Friedel–Crafts reaction conditions, it is commonly known as the Scholl reaction.[11] Two main types of mechanism have been suggested; one involves the initial formation of a very reactive transient cation radical followed by dimerization, and the other involves protonation of the aromatic molecule, followed by electrophilic substitution and subsequent dehydrogenation.[11] Because of the powerful electron releasing nature of alkoxy groups, the Scholl reaction has been widely utilized with alkyl aryl ether substrates.

The oxidation of 1,2-dialkoxybenzene to hexaalkoxy-TP (Scheme 1) is one of the unusual cases of Scholl reaction where more than one aryl-aryl bonds are formed. Oxidative trimerization of 1,2-dimethoxybenzene (veratrol) in H_2SO_4 using chloranil or iron chloride as oxidant results in the synthesis of hexamethoxytriphenylene (HMTP) involving three consecutive Scholl reactions.[11,12] When the six peripheral alkoxy chains are long enough (of four carbon atoms or more), triphenylene derivatives show mesomorphism. These long alkoxy chain substituted derivatives were prepared traditionally by demethylating HMTP and then realkylating the resultant hexaphenol with the appropriate alkyl halide.[7] A few triphenylene derivatives were also prepared in small scale by electrochemical methods.[13]

The use of $FeCl_3$ as oxidant was further explored by the Ringsdorf group, who reported the synthesis of hexahexyloxytriphenylene by the trimerization of 1,2-dihexyloxybenzene in 70% H_2SO_4 at 80 °C using iron chloride in 20% yield.[14] The modified method of the Boden group using only a catalytic amount of H_2SO_4 and iron chloride as oxidant allows the synthesis of triphenylene derivatives in a much improved scale.[15] Recently, we have reported that



Scheme 1

in addition to known chloranil and iron chloride, molybdenum(V) chloride[16] and vanadium oxytrichloride[10] can be utilized for the oxidative trimerization of 1,2-dialkoxybenzenes to hexaalkoxytriphenylenes in high yields. $VOCl_3$ is the only liquid oxidizing reagent so far reported for the synthesis of TP derivatives. It can be easily handled under anhydrous conditions using standard syringe technique or by using an addition funnel for large-scale preparation. The use of $VOCl_3$ in intramolecular oxidative phenolic couplings is well-documented[17] but its use in intermolecular couplings is not explored much.

When various 1,2-dialkoxybenzenes (**1a**–**g**) were treated with $VOCl_3$, hexaalkoxytriphenylenes (**2a**–**g**) were formed in high yields (Table 1). The reaction occurs under very mild conditions with or without any additional acid catalyst and in a very short time at room temperature (Scheme 1). $VOCl_3$ is miscible in various organic solvents and this could be a reason for the almost spontaneous trimerization of dialkoxybenzenes into hexaalkoxytriphenylenes. All the products were characterized from their spectral data, thermal behavior, and by direct comparison with authentic samples. Unlike the $FeCl_3$ method where catalytic amount of H_2SO_4 increases the product yield,[15] the $VOCl_3$ method does not require H_2SO_4. In fact its presence decreases the yield in many cases.

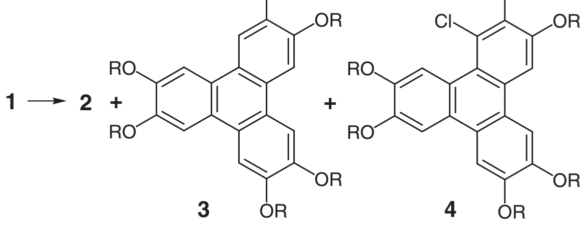
Table 1 Preparation of Triphenylene Derivatives using 2.5 equiv $VOCl_3$ in CH_2Cl_2 Solution at r.t.

Starting Material	Product	Yield %
1a	**2a**	53
1b	**2b**	86
1b	**2b**	79[a]
1c	**2c**	85
1c	**2c**	83[a]
1d	**2d**	56
1e	**2e**	70
1f	**2f**	70
1g	**2g**	65

[a] In the presence of 0.4% H_2SO_4.

Side Products of the Reaction

Currently three reagents, $FeCl_3$, $MoCl_5$, and $VOCl_3$ are in use for the oxidative trimerization of *o*-dialkoxybenzenes to hexaalkoxytriphenylenes. We realized that in all three cases two main side products are formed. These are monohydroxy-pentaalkoxy-TP **3** and α-chloro-hexaalkoxy-TP **4** (Scheme 2). Under normal reaction conditions about 2–3% of these products is formed. Both can be separated by efficient column chromatography and their amounts can be manipulated, if required, by varying reaction conditions. The α-chlorinated product has recently been prepared by chlorinating hexaalkoxy-TP with iodine monochloride.[18] The monohydroxy-pentaalkoxy-TP is a very valuable precursor for the synthesis of dimers, oligomers, side-chain polymers and networks. It can be prepared by several different ways[19] such as, a non-selective cleavage of one of the alkoxy chain of hexaalkoxy-TP by the use of a calculated amount of 9-Br BBN, or B-bromocatecholborane; by the partial alkylation of hexaacetoxy-TP to monoacetyl-TP followed by hydrolyses; a selective cleavage of the methyl ether of monomethoxypentaalkoxy-TP with lithium diphenylphosphide; or by direct coupling of a tetraalkoxybiphenyl with alkoxyphenol. By increasing the amount of H_2SO_4 (1–10%) in the reaction mixture, this compound can also be obtained up to 25% as a side product in the oxidative trimerization of dialkoxybenzene using $FeCl_3$, $MoCl_5$ or $VOCl_3$. In the absence of H_2SO_4, only traces of monohydroxy-pentaalkoxy-TP are formed. Dichlorinated-, trichlorinated-hexaalkoxy-TP and monochloro-dialkoxybenzene are the other side products formed in the reaction



Scheme 2

Effect of Reagent Concentration

To determine the optimum amount of $VOCl_3$ for the oxidative trimerization of dialkoxybenzenes to hexaalkoxy-TPs, we performed the reaction with 1,2-dibutyloxybenzene using variable amounts of $VOCl_3$ in CH_2Cl_2 (it was found to be the best solvent, see effect of solvent). The results are summarized in Table 2. Although only 2 equivalents of $VOCl_3$ are required to generate diradical cation species, the best yield of hexabutyloxy-TP was realized using 2.5 equivalents of $VOCl_3$. This could be due to the impurities present in the commercial reagent or non-per-

Table 2 Oxidative Coupling of 1,2-Dibutyloxybenzene in CH_2Cl_2 using Different Concentrations of $VOCl_3$ at r.t.

Substrate	$VOCl_3$ (mol equiv)	Product (yield, %)
1b	0.5	**2b** (28)
1b	1.0	**2b** (50)
1b	2.0	**2b** (76)
1b	2.5	**2b** (86)
1b	3.0	**2b** (45)

fect anhydrous reaction conditions. As expected, reducing the amount of the reagent decreases the product yield, but increasing the reagent concentration also decreases the yield of hexabutyloxy-TP. This could be because of the formation of side products. It should be noted that all the reactions were carried out under identical reaction conditions. Efforts have not been made to optimize various parameters associated with each reaction.

Effect of Solvent

Choice of reaction solvent has significant effects on the course of reaction. Oxidative coupling of phenols and phenol ethers has been reported in various solvents such as CH_2Cl_2, Et_2O, CH_3CN, CCl_4, etc. In order to find the best solvent for the preparation of triphenylene derivatives, we performed the trimerization of 1,2-dibutyloxybenzene using $VOCl_3$ in various solvents under identical reaction conditions. Typically, to a solution of 1.0 g of 1,2-dibutyloxybenzene in 5 mL of the appropriate solvent, was added slowly 2.5 equivalents of $VOCl_3$ and the mixture was stirred at room temperature for 5–10 min. After, it was quenched with methanol and extracted with H_2O/CH_2Cl_2. The crude product was purified by column chromatography. The results are summarized in Table 3. As indicated in Table 3, the best yield was realized using CH_2Cl_2 as a solvent. Reactions carried out in hexane and CCl_4 resulted in relatively low yield of hexabutyloxy-TP and produced a significant amount of monochloro-TP (**4**, about 39%). There was no hexabutyloxy-TP formation observed in THF, CH_3CN and HOAc. It is difficult to rationalize why other solvents result in poor yields of hexabutyloxy-TP.

Table 3 Oxidative Coupling of 1,2-Dibutyloxybenzene using 2.5 equiv $VOCl_3$ in Different Solvents

Substrate	Solvent	Product (yield, %)
1b	Hexane	**2b** (14)
1b	CH_2Cl_2	**2b** (86)
1b	CH_2Cl_2	**2b** (23)[a]
1b	THF	**2b** (0)
1b	CH_3CN	**2b** (0)
1b	AcOH	**2b** (0)
1b	CCl_4	**2b** (22)

[a] Performed at 0 °C.

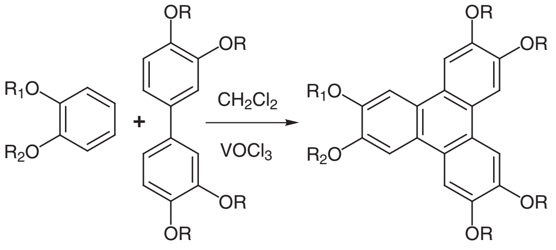
Effect of Temperature

When the reaction is carried out at 0 °C in CH_2Cl_2 using 2.5 equivalents of $VOCl_3$, hexabutyloxy-TP is formed in about 23% yield. About 50% of unreacted starting material and traces of monochloro-dibutyloxybenzene were isolated from this reaction. From the above results, it is clear that the use of 2.5 equivalents of $VOCl_3$ in dry CH_2Cl_2 at room temperature are the best reaction conditions for the trimerization of *o*-dialkoxybenzene to hexaalkoxy-TP. The presence of concentrated H_2SO_4 resulted in the cleavage of one or more alkoxy chains, while excess of the reagent yielded chlorinated side products.

Synthesis of Unsymmetrical Triphenylene Derivtives

To examine the effect of dissymmetry on the mesophase, Tinh et al. prepared several dissymmetrical hexasubstituted triphenylenes by putting different alkyl chains in the periphery and found that an introduction of non-symmetric side-chains does not affect the nature of Col_h phase, but results in the reduction of the mesophase stability.[20] Traditionally, these materials have been prepared by statistical approach involving either oxidative trimerization of a mixture of two different 1,2-dialkoxybenzene derivatives[20] or by partial alkylation of hexaacetoxytriphenylene followed by alkylation.[21] Unsymmetrical TP derivatives prepared by the introduction of a single ester side chain (monoalkanoyloxy-pentaalkoxy-TPs) show significant enhancement in the mesophase stability.[21b] A plastic columnar discotic phase is reported in these types of unsymmetric triphenylene derivatives.[22] A well defined but lengthy synthesis of unsymmetrically substituted TP derivatives was described by Wenz in 1985.[23] The incorporation of tetramethoxybiphenyl with veratrol to prepare HMTP was reported in 1965 by Musgrave.[24] Recent developments of this rational synthesis involving oxidative coupling of a tetraalkoxybiphenyl with dialkoxybenzene derivatives allowed production of these unsymmetrical derivatives in large amounts with high purity. A variety of unsymmetrical triphenylene discotics have recently been prepared following this process.[10,16,25-28] Organometallic chemistry has also been applied for the synthesis of unsymmetrical substituted triphenylenes.[29]

Unsymmetrically substituted TP derivatives **7a–c** were obtained from the oxidation of a mixture of **5a** or **5b** and 3,3′,4,4′-tetrabutyloxybiphenyl **6a** or tetrapentyloxybiphenyl **6b** with $VOCl_3$ in about 50% yield (Scheme 3). Cross coupling reaction leading to unsymmetrical TPs dominates over the oxidative dimerization of tetraalkoxybiphenyl or trimerization of dialkoxybenzene. In view of this efficient cross coupling, it has been suggested[11b,24] that tetraalkoxybiphenyl is probably the intermediate product during the oxidative trimerization of 1,2-dialkoxybenzene to hexaalkoxy-TP. However, we could not isolate any tetraalkoxybiphenyl in the oxidative trimerization of 1,2-dialkoxybenzene even when only 0.5 equivalent or lesser amount of the reagent was used, which resulted in lower yields of **2** along with appreciable amount of unreacted starting material. This indicates that the coupling occurs concomitant with a concerted two-electron transfer in the oxidative trimerization of 1,2-dialkoxybenzene to hexaalkoxy-TP.



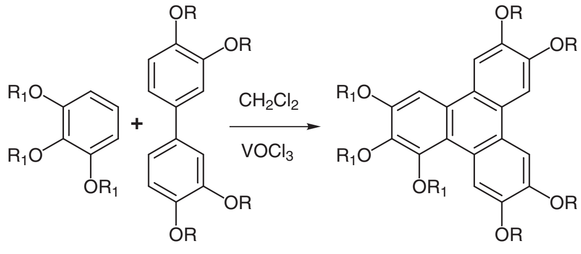
5 **6** **7**

a: $R = C_4H_9$, $R_1 = CH_3$, $R_2 = C_5H_{11}$
b: $R = R_2 = C_5H_{11}$, $R_1 = CH_3$
c: $R = C_5H_{11}$, $R_1 = R_2 = (CH_2)_2CH(CH_3)(CH_2)_3CH(CH_3)_2$

Scheme 3

Synthesis of Heptaalkoxytriphenylenes

Heptaalkoxy-TP discotic LCs are important as they possess lower clearing temperatures and broad mesophase ranges. We have recently reported the synthesis of heptaalkoxy-TPs by two different ways, one starting from monohydroxy-pentaalkoxytriphenylenes, and the other via biphenyl route using either $MoCl_5$ or $FeCl_3$ as oxidant.[30] We have found that the coupling of a tetraalkoxybiphenyl with a trialkoxybenzene works well using $VOCl_3$ as an oxidant (Scheme 4).



8 **9** **10**

a: $R = R_1 = C_4H_9$
b: $R = CH_3$, $R_1 = C_5H_{11}$
c: $R = C_4H_9$, $R_1 = C_2H_5$
d: $R = C_5H_{11}$, $R_1 = C_2H_5$
e: $R = C_5H_{11}$, $R_1 = C_4H_9$
f: $R = C_5H_{11}$, $R_1 = C_{12}H_{25}$

Scheme 4

When tetraalkoxybiphenyls **9** were reacted with trialkoxybenzenes **8**, heptaalkoxy-TPs **10** were formed (Table 4). Thus, heptaalkoxy-TPs having all the seven peripheral alkoxy chains identical or three different in size can be prepared efficiently.

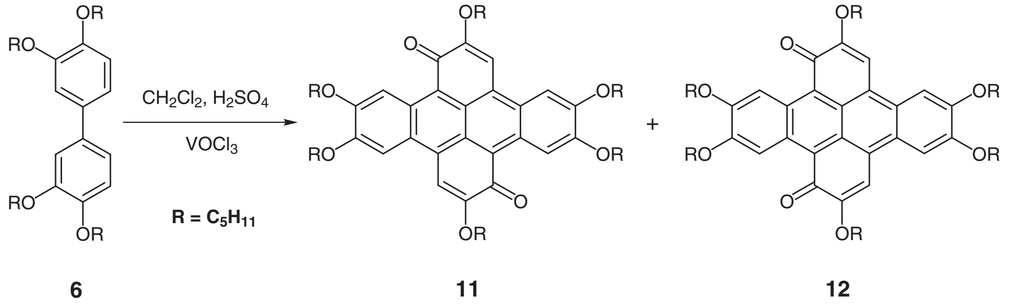
Table 4 Preparation of Heptaalkoxy-TP Derivatives using $VOCl_3$ in CH_2Cl_2 Solution at r.t.

Substrate	Product	Yield %
8a + 9a	**10a**	40
8b + 9b	**10b**	25
8c + 9c	**10c**	51
8d + 9d	**10d**	49
8e + 9e	**10e**	48
8f + 9f	**10f**	20

Oxidative Dimerization of Tetraalkoxybiphenyl

Discotic liquid crystals based on dibenzopyrene (DBP) have been the subject of many recent publications. Bock and Helfrich have demonstrated for the first time the existence of ferroelectricity in the columnar liquid crystals of 1,2.5,6,8,9,12,13-octakis-(*S*)-2-heptyloxypropanoyloxy)dibenzopyrene.[9,31] Synthesis of various octaalkoxy-substituted DBPs and their photophysical properties have been reported by the Ringsdorf and Markovitsi groups.[27b,32] Mesomorphic properties of five homologues of the 1,2,5,6,8,9,12,13-octaalkoxy-DBP and their charge transfer complexes with 2,4,7-trinitro-9-fluorenone are reported by S. Zamir et al.[33] The electro-optical and electromechanical effects in these materials were also reported very recently.[34,35]

All the DBP derivatives were prepared following the method of Musgrave and Webster[36] which involves the oxidation of 3,3′,4,4′-tetramethoxybiphenyl by chloranil in 70% sulfuric acid to 2,5,6,9,12,13-hexamethoxydibenzo[*fg,op*]naphthacene-1,8-quinone and its 1,10-quinone isomer. Reductive acetylation followed by alkylation resulted in the synthesis of 1,2,5,6,8,9,12,13-octasubstituted-DBP liquid crystals. Direct oxidation of tetrapentyloxybiphenyl by chloranil to hexapentyloxydibenzo[*fg,op*]naphthacene-1,8-quinone and its conversion to octapentyloxy-DBP by the above mentioned procedure has also been reported by the Ringsdorf group.[27b] We have found that $VOCl_3$ can be efficiently utilized under very mild reaction conditions for the preparation of two quinones. When 3,3′,4,4′-tetrapentyloxybiphenyl **6b** was treated with $VOCl_3$ in CH_2Cl_2 containing 0.5% concentrated H_2SO_4, 2,5,6,9,12,13-hexapentyloxydibenzo-1,8-quinone **11** and 2,5,6,9,12,13-hexapentyloxydibenzo-1,10-quinone **12** are formed in 24% and 50% yield, respectively (Scheme 5). Presence of concentrated H_2SO_4 is essential for the dimerization. In its absence, no product formation was observed. Although the purification of these quinones is extremely difficult, they can be separated by repeated column chromatography. The purity of the quinones can be monitored by ^1H NMR where the



Scheme 5

three singlets for aromatic protons appear relatively down field for the 1,10-quinone isomer (see experimental). Both the quinones can be converted to liquid crystalline derivatives using well-established chemistry.[27b] It should be noted that derivatives of only the 1,8-isomer, i.e., 1,2,5,6,8,9,12,13-octasubstituted-DBP have been reported in the literature. Derivatives of the 1,10-isomer, which has a different symmetry, have so far not been prepared. We are currently working on the synthesis of these derivatives.

Chemicals and solvents (AR quality) were obtained locally and used as such without any purification. Column chromatographic separations were performed on silica gel (70–230 and 200–400 mesh). TLC was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F_{254}). MS were recorded on a JEOL JMS-600H spectrometer in FAB+mode using *m*-NBA matrix. Elemental analysis was provided by Atlantic Microlab, Inc., U.S.A. ^{1}H NMR spectra were recorded on a 200 MHz and ^{13}C NMR spectra on a 500 MHz Bruker NMR spectrometer in $CDCl_3$. All chemical shifts (δ) are reported in ppm downfield from TMS, and *J* values are given in Hz. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMRXP polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin–Elmer). Peak temperatures observed in the heating and cooling runs of DSC have been reported.

Synthesis of Hexaalkoxy-TPs; General Procedure

To a solution of 1,2-dialkoxybenzene (0.005 mol) in dry CH_2Cl_2 (10 mL), $VOCl_3$ (0.013 mol) was added dropwise. The reaction mixture was stirred at r.t. for 5–10 min under N_2 atm. The reaction was quenched with MeOH (5 mL), poured over ice-water (20 mL) and extracted with CH_2Cl_2 (4 × 20 mL). The crude product was purified by repeated column chromatography over silica gel (hexane-CH_2Cl_2 mixtures). All the known products were characterized from their spectral data and phase behaviour. ^{1}H NMR data, mass and thermal behaviour of all the derivatives were found to be in accordance with the structure and literature data.[16,30,37] Spectral data and thermal behaviour of new compounds are given below.

2g:

Mp: 27 °C.

^{1}H NMR: δ = 7.85 (s, 6H), 4.27 (m, 12H), 2.00–1.20 (m, 60H), 1.03 (d, 18H, *J* = 6.5 Hz), 0.88 (d, 36H, *J* = 6.5 Hz).

^{13}C NMR: δ = 149.5, 124.1, 107.9, 68.5, 39.8, 37.9, 36.9, 30.5, 28.4, 25.2, 23.1, 23.0, 20.2.

MS: *m/z* = 1164.2.

Anal. Calcd for $C_{78}H_{132}O_6$: C, 80.35; H, 11.41. Found: C, 80.20; H, 11.48.

4b:

^{1}H NMR: δ = 9.06 (s, 1H), 7.79 (2 × s, 4H), 4.25 (m, 10H), 4.12 (t, 2H, *J* = 6.5 Hz), 1.92 (m, 12H), 1.60 (m, 12H), 1.0 (m, 18H).

^{13}C NMR: δ = 151.6, 150.3, 149.3, 148.8, 147.6, 146.1, 127.9, 126.1, 125.2, 125.1, 123.4, 123.3, 122.1, 112.3, 108.7, 107.6, 107.1, 105.7, 73.6, 70.1, 69.8, 69.6, 69.3, 69.2, 32.8, 31.9, 31.8, 19.8,14.3.

MS: *m/z* = 695.2.

Anal. Calcd for $C_{42}H_{59}ClO_6$: C, 72.54; H, 8.55; Cl, 5.10. Found: C, 72.49; H, 8.58; Cl, 5.13.

Thermal Behaviour: On first heating the compound melts at 55 °C to a highly ordered columnar mesophase that changes to col_h phase at 96 °C and finally clears at 112.2 °C. Upon cooling, col_h phase appears at 109.3 °C and converted to an unidentified col_x phase at 93 °C. The compound does not show any textural change down to r.t. However, on second heating, the compound shows all the three transitions at 55.9 °C, 96.3 °C and 112.3 °C. The low temperature mesophase in hexabutyloxy-TP derivatives has recently been reported to be more ordered and referred to as col_p phase.[38] The low temperature mesophase, which appeared at 93 °C on cooling this compound is probably the col_p phase, but x-ray studies have to be done to confirm this.

Synthesis of Unsymmetrical and Heptaalkoxy-TPs; General Procedure

A mixture of the appropriate tetraalkoxybiphenyl **6** or **9** (1 mmol) and 1,2-dialkoxybenzene **5** (2 mmol) or 1,2,3-trialkoxybenzene **8** (2 mmol) was dissolved in anhyd CH_2Cl_2. $VOCl_3$ (3.0 mmol) was added and the reaction was subjected to the procedure described above.

7a:

^{1}H NMR: δ = 7.85, 7.83 (s, 1H each), 7.81 (3 × s, 4H), 4.24 (m, 10H), 4.10 (s, 3H), 1.93 (m, 10H), 1.57 (m, 12H), 1.05 (m, 15H).

^{13}C NMR: δ = 149.5, 124.1, 123.8, 107.8, 106.8, 105.5, 69.8, 56.7, 31.9, 29.4, 28.7, 23.0, 19.8, 14.4.

MS: *m/z* = 633.0.

Anal. Calcd for $C_{40}H_{56}O_6$: C, 75.91; H, 8.92. Found: C, 75.89; H, 8.90.

Thermal Behaviour: The compound melts at 86.9 °C to col_h phase which clears at 110.4 °C. The DSC shows another weak transition at 68.1 °C (enthalpy 2.8 kJ mol^{-1}), which is clearly not the crystallization temperature and, therefore, the compound stays in another highly ordered columnar phase below this temperature. The DSC does not show the crystallization peak down to r.t. but the material is not shearable at r.t. Probably it transforms into a glassy state at lower temperature but the glass transition is not detected in DSC.

7c:

^{1}H NMR: δ = 7.84 (s, 6H), 4.25 (m, 12H), 2.00–1.20 (m, 44H), 1.05–0.90 (m, 30H).

^{13}C NMR: δ = 149.4, 124.0, 107.7, 70.1, 68.4, 39.7, 37.9, 36.8, 30.5, 29.6, 28.8, 28.4, 25.2, 23.1, 23.0, 20.2, 14.5.

MS: *m/z* = 885.7.

Anal. Calcd for $C_{58}H_{92}O_6$: C, 78.68; H, 10.47. Found: C, 78.52; H, 10.56.

Thermal Behaviour: The compound is liquid crystalline at r.t. It clears at 63 °C on heating. On cooling, the col$_h$ appears at 61 °C and stays down to r.t.

10b:
Mp: 138.1 °C.

^{1}H NMR: δ = 9.25 (s, 1H), 7.81 (s, 3H), 7.69 (s, 1H), 4.12 (m, 18H), 1.93 (m, 6H), 1.50 (m, 12H), 0.91 (m, 9H).

^{13}C NMR: δ = 152.3, 152.1, 149.7, 149.2, 148.5, 142.5, 126.8, 124.6, 124.2, 123.9, 123.7, 118.6, 110.0, 105.5, 104.7, 104.3, 102.1, 74.5, 69.2, 56.6, 56.5, 56.4, 56.3, 30.7, 30.6, 29.6, 28.9, 28.8, 28.6, 23.1, 23.0, 14.5.

MS: *m/z* = 606.4.

Anal. Calcd for $C_{37}H_{50}O_7$: C, 73.24; H, 8.31. Found: C, 72.88; H, 8.70.

10c:
Mp: 89.9 °C.

^{1}H NMR: δ = 9.24 (s, 1H), 7.83 (s, 2H), 7.81 (s, 1H), 7.69 (s, 1H), 4.25 (m, 14H), 1.93 (m, 8H), 1.56 (m, 17H), 1.04 (m, 12H).

^{13}C NMR: δ = 151.9, 150.0, 149.2, 148.9, 148.5, 142.3, 126.9, 125.0, 124.4, 124.1, 123.8, 118.7, 112.0, 108.6, 107.4, 102.6, 69.97, 69.81, 69.75, 69.66, 69.53, 69.25, 64.97, 31.9, 19.8, 16.4, 15.4, 14.4.

MS: *m/z* = 648.5.

Anal. Calcd for $C_{40}H_{56}O_7$: C, 74.04; H, 8.70. Found: C, 73.58; H, 8.66.

10d:
Mp: 82.6 °C.

^{1}H NMR: δ = 9.24 (s, 1H), 7.82 (s, 2H), 7.80 (s, 1H), 7.69 (s, 1H), 4.21 (m, 14H), 1.95 (m, 8H), 1.54 (m, 25H), 0.97 (t, 12H).

^{13}C NMR: δ = 151.93, 151.87, 149.9, 149.2, 148.8, 148.5, 142.3, 126.9, 125.0, 124.4, 124.1, 123.8, 118.7, 112.0, 108.5, 107.4, 102.6, 70.3, 70.0, 69.9, 69.8, 69.5, 65.0, 29.5, 28.8, 23.0, 16.4, 15.4, 14.5.

MS: *m/z* = 704.4.

Anal. Calcd for $C_{44}H_{64}O_7$: C, 74.96; H, 9.15. Found: C, 74.84; H, 9.37.

10e:
^{1}H NMR: δ = 9.22 (s, 1H), 7.83 (s, 2H), 7.81 (s, 1H), 7.67 (s, 1H), 4.21 (m, 12H), 4.03 (m, 2H), 1.90 (m, 14H), 1.54 (m, 22H), 1.02 (m, 21H).

^{13}C NMR: δ = 152.1, 149.9, 149.2, 148.8, 148.5, 142.3, 126.9, 125.0, 124.4, 124.1, 123.8, 118.6, 112.2, 108.7, 107.4, 102.1, 70.3, 70.0, 69.9, 69.7, 68.9, 33.1, 33.0, 31.9, 29.6, 28.8, 23.0, 19.8, 14.5.

MS: *m/z* = 789.4.

Anal. Calcd for $C_{50}H_{76}O_7$: C, 76.10; H, 9.71. Found: C, 76.44; H, 9.96.

Thermal Behaviour: The compound is found to be liquid crystalline at r.t. On heating it clears at 65 °C. The col$_h$ appears at 63 °C on cooling and stays down to r.t.

10f:
Mp: 67 °C.

^{1}H NMR: δ = 9.20 (s, 1H), 7.82 (s, 2H), 7.80 (s, 1H), 7.66 (s, 1H), 4.20 (m, 14H), 1.90 (m, 14H), 1.50−1.20 (m, 70H), 0.93 (m, 21H).

^{13}C NMR: δ = 152.2, 150.0, 149.3, 148.9, 148.6, 142.4, 126.9, 125.0, 124.4, 124.2, 123.9, 118.6, 112.3, 108.9, 107.6, 102.3, 74.5, 74.4, 70.4, 70.1, 70.0, 69.7, 69.3, 32.3, 31.2, 31.1, 31.0, 30.1, 29.9, 29.8, 29.6, 29.5, 28.8, 26.7, 26.6, 23.1, 22.9, 14.5.

MS: *m/z* = 1125.0.

Anal. Calcd for $C_{74}H_{124}O_7$: C, 78.95; H, 11.10. Found: C, 79.33; H, 11.27.

Oxidative Dimerization of Tetraalkoxybiphenyl

3,3′,4,4′-Tetrapentyloxybiphenyl **6** (1 mmol) was dissolved in anhyd CH_2Cl_2 (10 mL) containing 0.5% concd H_2SO_4. $VOCl_3$ (2.5 mmol) was added and the reaction was stirred at r.t. for 15 min. It was then poured over ice-water (20 mL) and extracted with CH_2Cl_2 (4 × 20 mL). The black crude product was purified by repeated column chromatography over silica gel (hexane: CH_2Cl_2, 6:4) to afford 2,5,6,9,12,13-hexapentylkoxydibenzo[*fg,op*]naphthacene-1,8-quinone (**11**, 24%)[27b] and 2,5,6,9,12,13-hexapentylkoxydibenzo[*fg,op*]naphthacene-1,10-quinone (**12**, 50%).

11:
^{1}H NMR: δ = 9.36 (s, 2H), 7.32 (s, 2H), 7.13 (s, 2H), 4.20 (m, 12H), 1.98 (m, 12H), 1.50 (m, 24H), 1.00 (m, 18H).

^{13}C NMR: δ = 181.4, 155.5, 153.3, 150.3, 131.6, 131.1, 128.4, 119.3, 106.2, 105.3, 102.2, 68.8, 68.6, 28.8, 28.4, 22.6, 14.1.

MS: *m/z* = 848.9.

12:
^{1}H NMR: δ = 9.47 (s, 2H), 7.39 (s, 2H), 7.20 (s, 2H), 4.20 (m, 12H), 1.98 (m, 12H), 1.50 (m, 24H), 1.00 (m, 18H).

^{13}C NMR: δ = 181.5, 155.6, 153.4, 150.4, 131.8, 131.3, 128.5, 119.2, 106.3, 105.4, 102.3, 68.9, 68.7, 28.8, 28.3, 22.6, 14.1.

MS: *m/z* = 848.9.

Anal. Calcd for $C_{54}H_{72}O_8$: C, 76.38; H, 8.55. Found: C, 76.44; H, 8.70.

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