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Rational Synthesis of Bis(hexyloxy)-Tetra(hydroxy)-Triphenylenes and their Derivatives.

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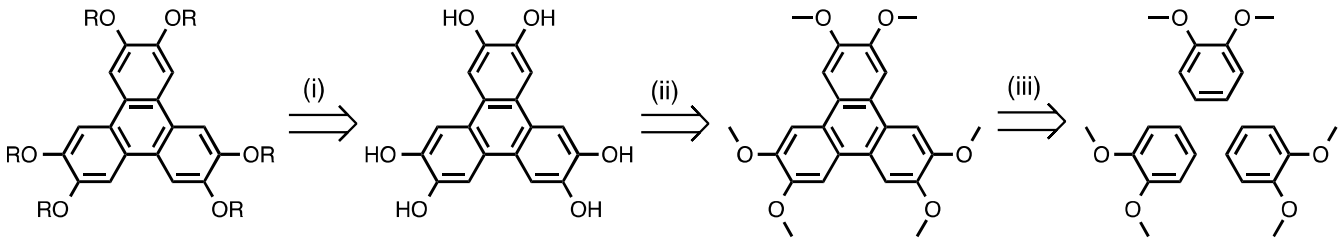
Abstract

A straightforward, reliable, and scalable synthesis of rationally designed, mixed-substituent triphenylene derivatives from *ortho*-terphenyl precursors is described. Three isomers of bis(hexyloxy)-tetrahydroxy triphenylenes were synthesized and functionalized with monomethyl di(ethylene glycol) chains to provide new amphiphilic, mixed substituent triphenylenes. Oxidative triphenylene annulation, tetra-ol formation, and subsequent functionalization were supported by significant changes in phase and melting point, and confirmed by mass spectrometry, differential scanning calorimetry, and UV/Vis, ^{1}H, and ^{13}C NMR spectroscopies. The thermal phase properties of amphiphilic mixed-substituent triphenylene derivatives were found to vary between the different isomers, demonstrating how small changes in substitution pattern can result in significant differences in mesogenic behavior. The controlled synthetic route to *de novo* designed triphenylene derivatives is dependable, wide in scope, and can be applied to the synthesis of a vast array of other mixed-substituent triphenylene derivatives, thus enabling the preparation of libraries of novel triphenylene and triphenylene-containing materials.

Introduction

Polycyclic aromatic triphenylene derivatives are well-known for their mesogenic behavior.[1] Examples of over 500 discotic liquid crystals incorporating a triphenylene core have been reported in the literature.[2,1c] The delocalized 18 π-electron system and high thermal and chemical stabilities[3] of triphenylenes make them well-suited as components in optoelectronic[4], photoconductive[5], and electroluminescent[6] materials, with potential applications as liquid crystalline semiconductors.[7] Typically, mesogenic triphenylenes are functionalized with alkyl groups at their periphery to facilitate columnar phase assembly through a combination of aliphatic van der Waals interactions and aromatic π-π stacking of triphenylene cores.[1,3a,8] In particular, triphenylene assembly is enhanced by the six-fold substitution of medium length alkyloxy chains at the 2, 3, 6, 7, 10, and 11 positions.[9] Synthetic routes toward six-fold substituted triphenylenes are well-established,[3b,10] and symmetric triphenylenes have been prepared with a variety of substituents, including alkyl chains,[1c] esters,[2a,11] thioesters,[7a,12] and benzyl ether[2b,13] moieties. Most commonly, symmetric hexa-substituted triphenylenes have been prepared by the alkylation of 2,3,6,7,10,11-hexahydroxytriphenylene, which is prepared from the demethylation of 2,3,6,7,10,11-hexamethoxytriphenylene (Scheme 1).[1]

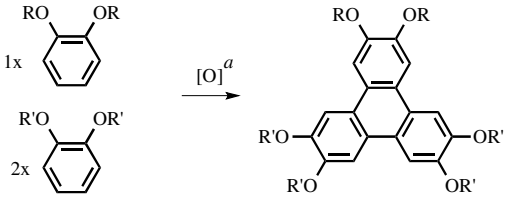
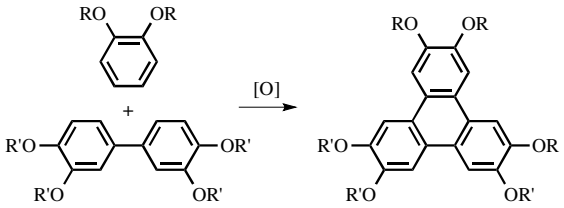
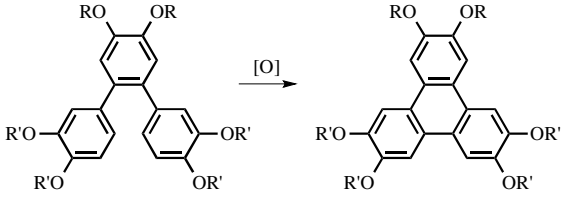


Scheme 1. Common retrosynthetic route to symmetrically substituted triphenylene mesogens: (i) alkylation, (ii) O-demethylation, (iii) oxidative trimerization.

While synthetic routes to symmetric triphenylenes are well established, there are few reliable and scalable synthetic routes to asymmetric or mixed-substituent triphenylene derivatives that are not complicated by the formation of closely related byproducts. This is despite the fact that such compounds

are increasingly desirable as varying the substituents at precise locations on the triphenylene core can affect their mesogenic behavior and lead to new and unique materials properties.[14] Synthetic routes reported to produce mixed-substituent 2, 3, 6, 7, 10, 11 substituted triphenylenes typically rely on oxidative trimerization, dimerization,[15] or annulation[16] of substituted aryl systems (Table 1). Originally, mixed substituent or asymmetric triphenylenes were prepared by oxidative trimerization of substituted catechols using chloranil and acid,[10b,15] but the low yields of desired products prompted the development of new methods. Oxidative Scholl annulations of differently substituted catechols (Table 1, entry A) or catechols and biphenyls (Table 1, entry B) using agents such as $FeCl_3$ and $MoCl_5$ have provided routes to mixed-substituent triphenylenes.[17,18] These pathways, however, require a large stoichiometric excess of oxidant and often result in undesirable side products that can be difficult or impossible to separate. Tricyclic *ortho*-terphenyl precursors (Table 1, entry C) eliminate triphenylene-based side products and require fewer equivalents of oxidant,[4a,18] making them attractive target compounds for asymmetric triphenylene synthesis. *Ortho*-terphenyl precursors of mixed-substituent triphenylene derivatives, however, typically require a greater number of synthetic steps to prepare.

Table 1. Summary of general synthetic routes to mixed-substituent triphenylene derivatives including oxidative trimerization of different catechol derivatives (entry **A**), oxidative dimerization of a catechol derivative with substituted biphenyls (entry **B**), and oxidative annulation of *ortho*-terphenyl derivatives bearing different substituents (entry **C**).

Entry	Scheme
A	
B	
C	

[a]Oxidative trimerization and dimerization reactions are commonly carried out using oxidants such as chloranil or Lewis acids such as $FeCl_3$, $MoCl_5$, $VoCl_3$, etc. The annulation of *ortho*-terphenyl derivatives has been carried out using these transition metal oxidants or anion-catalyzed TBAF ring closure.

An alternative route to mixed triphenylene derivatives can involve the selective alkylation of triphenylene poly-ols in a manner analogous to the synthesis of symmetric triphenylene derivatives from triphenylene hexaol as shown in Scheme 1. To that end, selectively substituted triphenylene mono and poly-ols are valuable precursors to mixed-substituent triphenylenes. Care must be taken to design appropriate synthetic routes to triphenylene poly-ols as catechol protecting groups must be both stable to

oxidative conditions used in the construction of the central triphenylene core, and easily and orthogonally removed to reveal the desired triphenylene poly-ol. As such, examples of routes to non-saturated triphenylene poly-ols are limited in scope and methodology. Mono-, di-, and tri-ols have been reported, but many have been synthesized through non-selective means.[19] Ringsdorf and co-workers, for example, have prepared penta-substituted triphenylene mono-ols by the partial cleavage of alkoxy groups from hexa-substituted triphenylenes using 9-Br-BBN.[20] The alkyl cleavage, however, was non-selective. Bushby and Lu reported a rational route to mono- and di-hydroxy triphenylenes by using isopropyl substituents to mask hydroxyl groups in the $FeCl_3$-oxidized dimerization of selectively substituted catechols and biphenyls.[21] Another selective route reported by Kumar and Manickam relied upon bromocatecholborane to cleave one, two, or three pentyl substituents from hexakis(pentyloxy) triphenylene resulting in the desired mono-, di-, and tri-ol products but yields were variable (17%-70%) and the authors noted difficult purifications.[22] In general, it is evident that the synthetic methods used to produce unsaturated triphenylene poly-ols tend to be harsh and non-selective, making the controlled synthesis of triphenylene tetra-ols particularly challenging. A reliable, controlled, scalable route to prepare rationally designed triphenylene poly-ol compounds is needed to fully explore the full variability and utility of mixed-substituent mesogenic triphenylene materials.

Our interest in the synthesis of triphenylene tetra-ols arose from our desire to prepare triphenylene derivative **1** (Figure 1) for use in dynamically assembled boronate ester materials. The dynamic self-assembly of catechol derivatives with boronic acids to form boronate esters has recently received increasing attention due to the development of structurally precise, highly porous covalent organic frameworks (COFs).[23] Along similar lines we have sought to design and self-assemble a variety of discrete, soluble analogues of COFs.[24] Such analogues would allow us to investigate the mechanism of COF assembly in solution and the properties of boronate ester mesogens. Triphenylene tetra-ol **1**, for example, can serve as a precursor to a discrete analogue of the widely studied COF-5 framework.[25] In developing a convenient synthetic route to **1** it became evident that similar synthetic routes could be

used to prepare a variety of differently substituted triphenylene tetra-ols. Herein we report the reliable synthesis of three isomers of tetra(hydroxy) triphenylene derivatives (**1**-**3**) as well as their functionalization with monomethyl di(ethylene glycol) chains to give three new amphiphilic, mixed substituent triphenylenes (**4**-**6**), which provide an opportunity to investigate the influence of regioisomerism on the thermal properties of mixed substituent triphenylene derivatives.

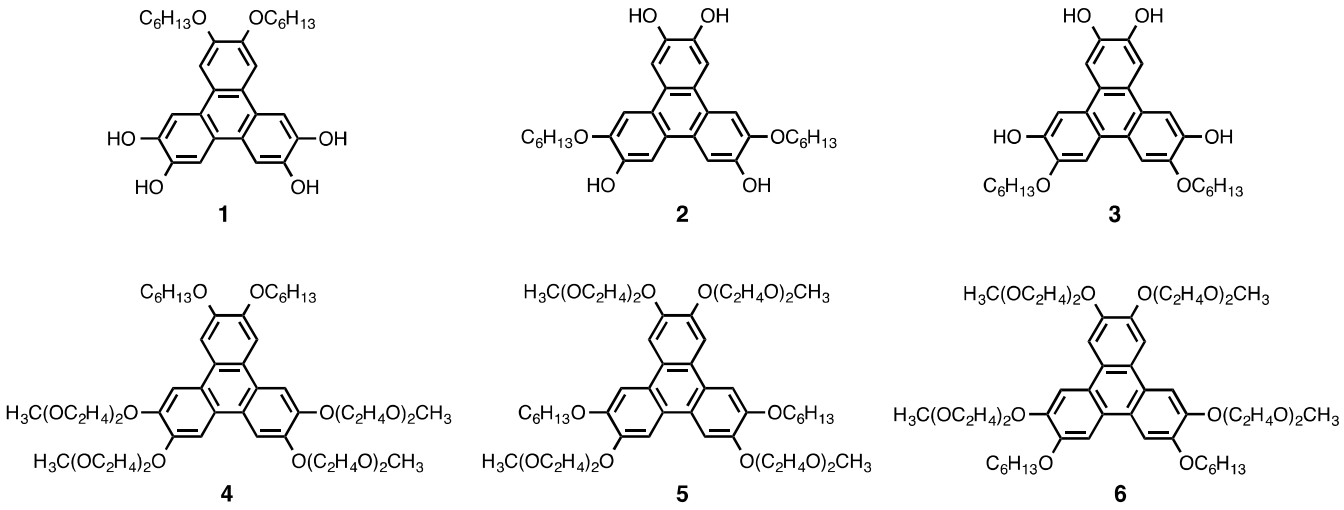


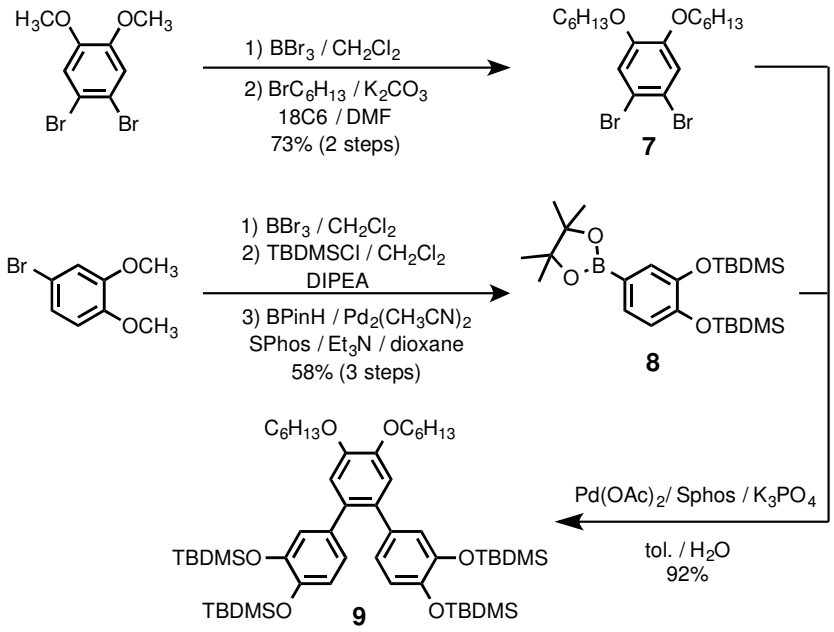
Figure 1. Chemical structures of target bis(hexyloxy)-tetra(hydroxy) triphenylene derivatives **1**-**3** and their corresponding amphiphilic derivatives **4**-**6**, which have been functionalized with monomethyl di(ethylene glycol) substituents.

Results and Discussion

Synthesis

Initial attempts at the synthesis of **1** involved the oxidative dimerization of symmetric and asymmetric substituted biphenyl compounds with functionalized catechols, employing a variety of protecting groups, transition metal oxidants, and reaction conditions. In all cases the desired product was either not observed or obtained in low yield and purification was complicated by the prevalence of undesired byproducts. Attention was therefore turned to the synthesis of *ortho*-terphenyl compounds that would likely undergo more selective and controlled annulation to desired triphenylene derivatives. Toward this

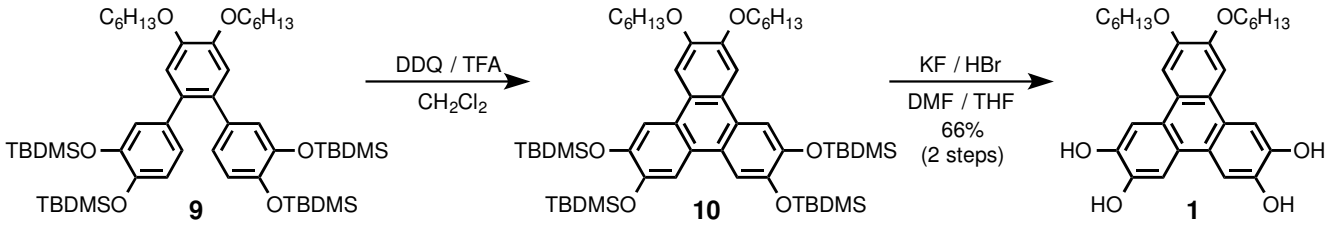
end *ortho*-terphenyl derivative **9** was prepared by Suzuki-Miyaura[26] coupling of 4,5-dibromo-1,2-bishexyloxy benzene **7** and bis(*tert*-butyldimethylsilyl) (TBDMS) protected aryl pinacolborane **8** (Scheme 2). Precursors **7** and **8** were prepared from 4,5-dibromoveratrole and 4-bromoveratrole in two and three steps, respectively.



Scheme 2. Synthesis of *ortho*-terphenyl **9** from the palladium-catalyzed cross-coupling of bishexyloxy-substituted benzene dibromide **7** and bis(*tert*-butyldimethylsilyl) protected aryl pinacolborane **8**.

Kumar and coworkers have previously reported that treatment of a related methoxy-substituted *ortho*-terphenyl derivative with tetra-butyl ammonium fluoride (TBAF) results in the sequential deprotection of the TBDMS moieties and subsequent annulation to give tetra(hydroxy) triphenylene derivatives.[27] Attempts to adapt this TBAF-promoted deprotection/annulation, while promising at preparative scales and when hexyloxy chains were replaced with methoxy substituents, were unsuccessful when run at larger scales or when applied to compound **9**. Alternative conditions for oxidative annulation were then explored. Rathore and others have shown that oxidative cyclodehydrogenation of various Scholl precursors can be carried out efficiently and in high yields using a mixture of dichlorodicyano-*p*-benzoquinone (DDQ) and an acid.[28] Indeed, reacting *ortho*-terphenyl compound **9** and stoichiometric DDQ in a 10:1 mixture of dichloromethane/TFA gave

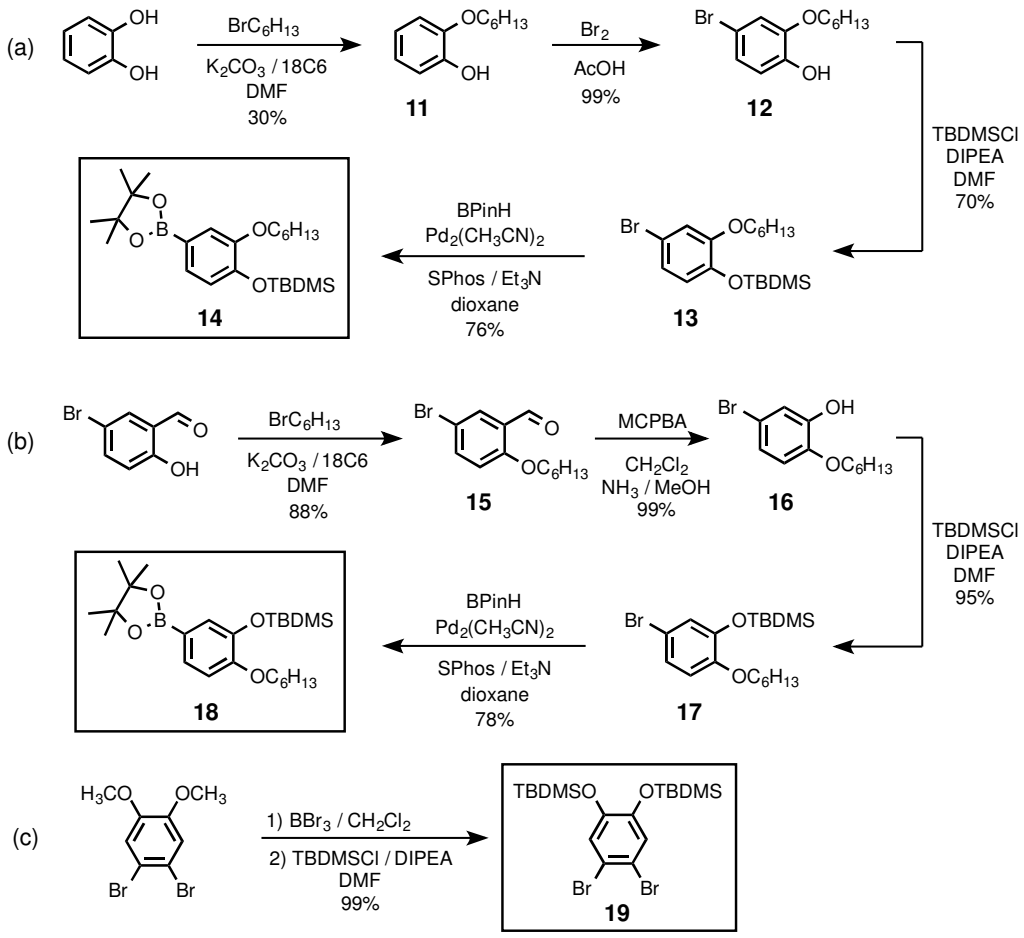
annulated triphenylene derivative **10** in good yield (Scheme 3). Subsequent deprotection of the four TBDMS groups at positions 6, 7, 10, and 11 with KF and HBr resulted in the desired 2,3-bis(hexyloxy)-6,7,10,11-tetrahydroxy triphenylene **1**. The overall synthetic route to triphenylene tetra-ol **1** outlined in Schemes 2 and 3 has several notable advantages over previous routes to triphenylene poly-ols, namely (i) it avoids the production of alternative triphenylene byproducts, (ii) the number and location of hydroxyl functionalities in the product are controlled precisely, and (iii) the route can be easily and reliably scaled to gram quantities.



Scheme 3. Successful annulation of *ortho*-terphenyl derivative **9** to triphenylene derivative **10** followed by subsequent TBDMS deprotection to give triphenylene tetra-ol **1**.

Given the reliability of the synthetic route to triphenylene tetra-ol **1** it became apparent that the synthesis could be readily adapted to the preparation of additional triphenylene tetra-ol isomers **2** and **3** (Figure 1). The key synthetic intermediates along the routes to tetra-ols **2** and **3** are uniquely substituted *ortho*-terphenyl derivatives, which can be similarly prepared from Suzuki-Miyaura couplings of aryl pinacolboranes and aryl dihalides that are different variations of compounds **7** and **8** (Scheme 2). The choice of substituents in the pinacolborane and dihalide precursors precisely determines the substituent pattern in their final triphenylene tetra-ols. Scheme 4 summarizes the synthetic routes to the three synthetic precursor compounds **14**, **18**, and **19**. Aryl pinacolboranes **14** and **18** are isomers of each other that differ only in the placement of their hexyloxy and *tert*-butyldimethylsilyloxy (OTBDMS) groups: in compound **14** the hexyloxy and OTBDMS substituents are *meta* and *para* to the pinacolborane, respectively, while in compound **18** the hexyloxy substituent is *para* to the pinacolborane and the OTBDMS is *meta*. The synthesis of compound **14** (Scheme 4a) requires statistical alkylation of catechol

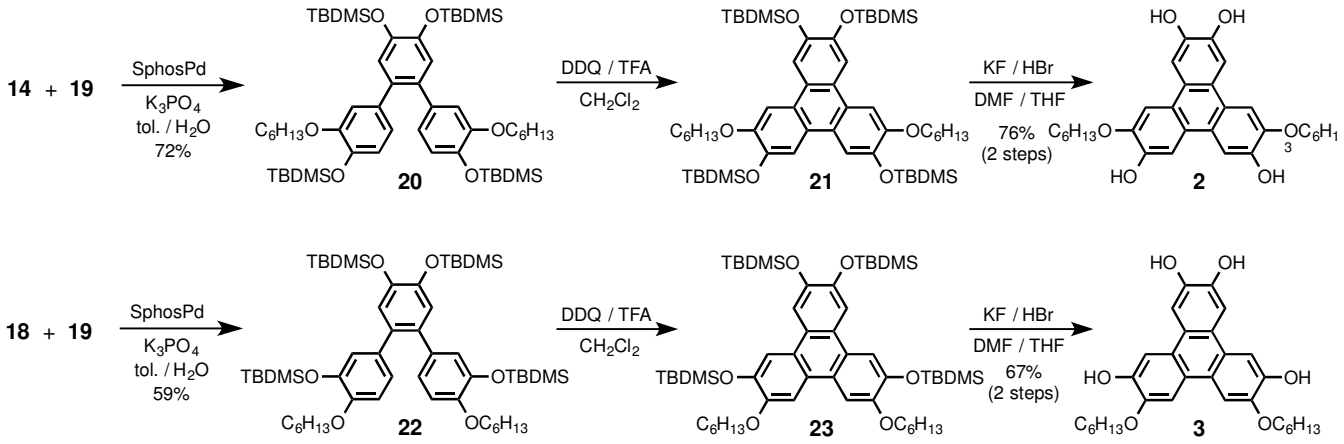
(**11**) followed by bromination (**12**)[29], protection with TBDMS (**13**), and ultimately borylation using conditions developed by Buchwald.[30] Compound **18** was synthesized along a related but slightly different route (Scheme 4b), starting with the alkylation[31] of 5-bromosalicylaldehyde to give **15**, Baeyer-Villiger rearrangement[32] to give the alcohol **16**, protection with TBDMS to provide **17**, and finally borylation.[30] The third key precursor shown in Scheme 4c is di(*t*-butyldimethylsilyloxy) dibromide **19**, which is easily prepared in two steps from dibromoveratrole.[12]



Scheme 4. Synthetic routes to two isomeric aryl pinacolboranes **14** (a) and **18** (b), each of which are catechol derivatives possessing one hexyloxy substituent and one *tert*-butyldimethylsilyloxy group. Shown in (c) is the synthesis of bis(*tert*-butyldimethylsilyloxy) dibromide **19**.

With compounds **14**, **18**, and **19** at hand the preparation of triphenylene tetra-ols **2** and **3** (Scheme 5) follows the same general method as the preparation of isomeric triphenylene tetra-ol **1**. Suzuki-Miyaura

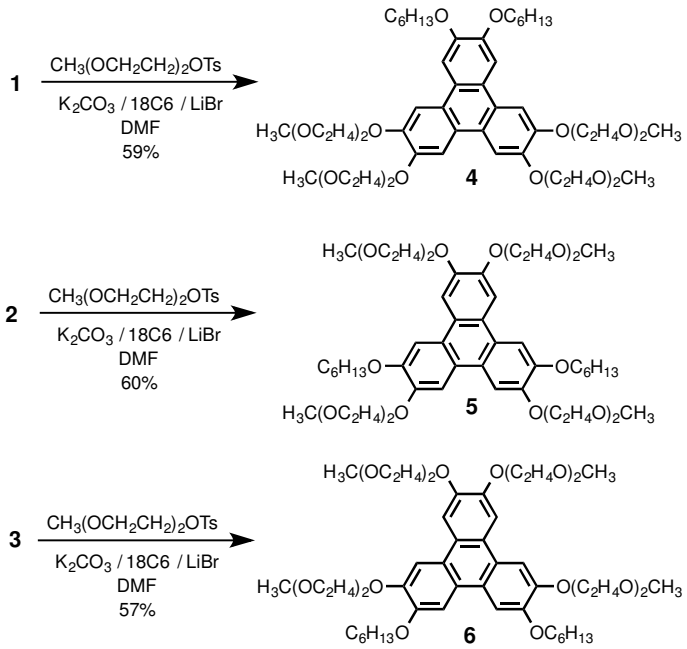
coupling of **14** and **19** gives *ortho*-terphenyl **20**. Oxidative annulation of **20** with DDQ in the presence of TFA results in tetra(*tert*-butyldimethylsilyloxy) triphenylene derivative **21**, which is subsequently deprotected with KF in HBr to provide 2,7-bis(hexyloxy)-3,6,10,11-tetrahydroxy triphenylene **2**. Likewise, palladium-catalyzed coupling of **18** and **19** gives *ortho*-terphenyl derivative **22**. DDQ oxidation of **22** in TFA/dichloromethane gives annulated tetra(*tert*-butyldimethylsilyloxy) product **23**. The TBDMS protecting groups of **23** are deprotected with KF and HBr to give 3,6-bis(hexyloxy)-2,7,10,11-tetrahydroxy triphenylene **3**. While the syntheses of isomeric triphenylene tetra-ols **1**-**3** each require 8 linear synthetic steps the reactions proceed, with one exception,[33] in good to excellent yields (59-99%) and are completely selective, providing highly controlled synthetic routes to precisely functionalized triphenylene tetra-ols.



Scheme 5. Synthesis of isomeric triphenylene tetra-ols **2** and **3** from precursors **14** and **19** or **18** and **19**, respectively, following the synthetic route involving Suzuki-Miyaura coupling, oxidative annulation, and TBDMS deprotection.

Triphenylene tetra-ols **1**-**3** are able to serve as versatile platforms for the preparation of mixed-substituent triphenylene derivatives. As representative examples of the ease with which hydroxyl functionalities of compounds **1**-**3** can be functionalized we have prepared mixed-substituent amphiphilic triphenylene derivatives **4**-**6** (Scheme 6). In each case, all four hydroxyl groups were successfully

substituted with di(ethylene glycol) monomethyl ether tosylate[34] in moderate yields. The versatility of the synthetic route presented herein should be reiterated, as any substituent with suitably electrophilic character could be used at this stage to provide libraries of mixed-substituent triphenylene derivatives. With rational routes to amphiphilic triphenylenes **4**-**6**, where the relative locations of hexyl and monomethyl di(ethylene glycol) substituents along the triphenylene core is completely controlled. Di(ethylene glycol) substituents were chosen because they are known to crystallize less readily than comparable length alkyl substituents. By substituting triphenylene cores with two substituents that favor crystallization (i.e. hexyloxy) and four that disfavor crystallization (i.e. monomethyl di(ethylene glycol)) we are able to investigate how the thermal and physical properties of mixed-substituent triphenylenes vary between different regioisomers.



Scheme 6. Functionalization of triphenylene tetra-ols **1**-**3** with hydrophilic monomethyl di(ethylene glycol) substituents to give mixed-substituent triphenylene derivatives **4**-**6**.

Experimental

Materials. Chemicals were obtained from commercial sources and used as received. Reagent-grade solvents were used as obtained from commercial sources. Anhydrous solvents were dried using an Innovative Technologies SPS-400-5 solvent purification system.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Mercury (300 MHz and 75 MHz, respectively) spectrometer using residual solvent as the internal standard. All chemical shifts are quoted using the δ scale and all coupling constants are expressed in Hertz (Hz). UV/Vis spectroscopy was recorded on a Varian Cary 100 Bio UV-Visible spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q20. The DSC is equipped with an RCS90 cooling system. DSC traces were acquired at rates of 10 °C/min (heating) and 5°C/min (cooling) in the temperature range of (-50)-100 °C. ESI/APCI and APCI-MS analysis was carried out at the University of California, Riverside, Mass Spectrometry Facility.

General *ortho*-terphenyl Preparation: To a heavy-walled glass reaction vessel was added aryl dihalide (1 eq), aryl pinacolborane (3 eq), and potassium phosphate (4 eq). The vessel was flushed with nitrogen, and SPhos Buchwald ligand (4 mol%) and palladium acetate (2 mol%) were added in that order. The vessel was further evacuated and backfilled with nitrogen (3x), and degassed 10:1 toluene:water mixture was added. The vessel was quickly sealed with a Teflon screw cap and was heated to 100°C overnight. The dark reaction mixture was allowed to cool, diluted with ether, and passed through a pad of Celite. The filtrate was concentrated under reduced pressure and purified by column chromatography to afford pure product.

Compound 9: Reaction Scale: Compound **7** (1.5 g, 3.44 mmol). The pure product eluted from the column with 20% dichloromethane in hexanes, and was isolated as a pale yellow oil (3.0 g, 92%). APCI-MS (m/z) $[MH]^+$ calculated for $C_{54}H_{95}O_6Si_4$, 951.6200: found 951.6180. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (s, 2H), 6.61 - 6.67 (m, 4H), 6.52-6.57 (dd, J = 8.8, 2.6 Hz, 2H), 4.04 (t, J = 6.6 Hz, 4H), 1.79-1.90 (m, 4H), 1.42-1.53 (m, 4H), 1.31-1.39 (m, 8H), 0.98 (m, 18H), 0.94 (s, 18 H), 0.90 (t, J = 5.3

Hz, 6H), 0.19 (s, 12H), 0.08 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 147.9, 146.1, 145.3, 135.1, 132.7, 122.8, 122.5, 120.2, 116.1, 69.3, 31.6, 29.3, 26.1, 25.9, 25.7, 22.6, 18.4, 14.1, -4.1, -4.2 ppm.

Compound 20: Reaction scale: Compound **19** (144 mg, 0.291 mmol). The pure product eluted from the column with 10% dichloromethane in hexanes, and was isolated as a white solid (199 mg, 72%). Mp = 146.0-147.8 °C. ESI/APCI (m/z) $[MH]^+$ calculated for $C_{54}H_{95}O_6Si_4$, 951.6200: found 951.6200. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.67 (s, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 7.9 Hz, 2H), 6.89 (s, 2H), 4.00 (t, J = 6.5 Hz, 4H), 2.11-2.02 (m, 4H), 1.83-1.74 (m, 4H), 1.75-1.66 (m, 8H), 1.43 (s, 18H), 1.40 (s, 18H), 1.31 (t, J = 6.5 Hz, 6H), 0.66 (s, 12H), 0.54 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 149.6, 145.6, 143.2, 135.1, 133.6, 122.8, 121.5, 120.2, 115.1, 68.2, 31.6, 29.3, 26.0, 26.0, 25.7, 25.7, 22.6, 18.4, 14.1, -4.0, -4.7 ppm.

Compound 22: Reaction scale: Compound **19** (110 mg, 0.223 mmol). The pure product eluted from the column with 10% dichloromethane in hexanes, and was isolated as a colorless semi-solid (124 mg, 59%). ESI/APCI (m/z) $[MH]^+$ calculated for $C_{54}H_{95}O_6Si_4$, 951.6200: found 951.6196. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.81 (s, 2H), 6.67-6.57 (m, 6H), 3.89 (t, J = 6.5 Hz, 4H), 1.83-1.74 (m, 4H), 1.51-1.43 (m, 4H), 1.36-1.28 (m, 8H), 1.02 (s, 18H), 0.96 (s, 18H), 0.92 (t, J = 7.0 Hz, 6H), 0.25 (s, 12H), 0.07 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 149.1, 145.5, 144.1, 134.1, 133.2, 123.0, 122.4, 112.3, 68.3, 31.7, 29.5, 26.0, 25.7, 22.6, 18.4, 14.1, -4.0, -4.7 ppm.

General triphenylene preparation: Two methods were used to prepare tetra(hydroxy) triphenylene derivatives from their appropriate *ortho*-terphenyl precursors. In a two-step procedure (Method A) tetra-TBDMS protected triphenylene intermediates **10**, **21**, and **23** were isolated and purified prior to TBDMS deprotection to allow full characterization of the tetra-TBDMS protected triphenylene derivatives. Alternatively, a one-step procedure (Method B) can be used wherein the intermediate is not isolated but rather carried directly through to deprotection following annulation. Method B was observed to both maximize the yield of the desired tetra-ol product and simplify the synthesis of **1**-**3**.

Method A: General annulation procedure: To a 0.01 M solution of *ortho*-terphenyl in dry dichloromethane was added neat trifluoroacetic acid (10% with respect to volume of solvent), and the solution stirred for 30 minutes at room temperature. Oxidant 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.1 equivalents) was added at 0 °C, and the solution was allowed to return slowly to room temperature over 3 hours; accompanied by a color change from pale lime green to emerald. Water was added slowly, and the crude product was extracted with dichloromethane (3x). The combined red or purple organic layers were washed with saturated sodium bicarbonate (3x) and brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting material was purified through a short pad of silica, eluting with 2.5% ethyl acetate in hexanes to afford the pure triphenylene derivatives.

Compound 10: Reaction scale, *ortho*-terphenyl **9** (700 mg, 0.736 mmol). The organic extracts were red, and the product was isolated as a pale pink semi-solid (323 mg, 46%). APCI-MS (m/z) $[MH]^+$ calculated for $C_{54}H_{93}O_6Si_4$, 949.6044: found 949.6027. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (s, 2H), 7.79 (s, 2H), 7.74 (s, 2H), 4.22 (t, *J* = 6.4 Hz, 4H), 1.99-1.88 (m, 4H), 1.33-1.26 (m, 12H), 1.08 (s, 18H), 1.07 (s, 18H), 0.93 (t, *J* = 6.74 Hz, 6H), 0.31 (s, 12H) 0.31 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 148.7, 146.6, 124.0, 123.2, 114.0, 106.8, 69.3, 31.7, 29.2, 26.1, 26.1, 25.9, 25.8, 22.7, 18.7, 14.1, -4.0, -4.1 ppm.

Compound 21: Reaction scale, *ortho*-terphenyl **20** (199 mg, 0.209 mmol). The organic extracts were a ruby red, and the product was isolated as a pale yellow solid (56 mg, 29%). Mp = 132.7-134.2°C. ESI/APCI (m/z) $[MH]^+$ calculated for $C_{54}H_{93}O_6Si_4$, 949.6044: found 949.6031. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.86 (s, 2H), 7.80 (s, 2H), 7.71 (s, 2H), 4.16 (t, *J* = 6.5 Hz, 4H), 1.98-1.89 (m, 4H), 1.63-1.53 (m, 4H), 1.44-1.34 (m, 8H), 1.10 (s, 18H), 1.08 (s, 18H), 0.95 (t, *J* = 5.6 Hz, 6H), 0.32 (s, 12H), 0.27 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 150.2, 146.5, 144.9, 124.2, 123.8, 123.2, 114.1, 105.8, 68.6, 31.7, 29.4, 26.1, 25.9, 25.8, 22.7, 18.7, 14.1, -4.0, -4.1 ppm.

Compound 23: Reaction scale, *ortho*-terphenyl **22** (200 mg, 0.210 mmol). The organic extracts were deep purple, and the product was isolated as a violet grey solid (144 mg, 72%). Mp = 131.4-133.6°C.

ESI/APCI (m/z) $[MH]^+$ calculated for $C_{54}H_{93}O_6Si_4$, 949.6044: found 949.6034. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.80 (s, 2H), 7.79 (s, 2H), 7.76 (s, 2H), 4.19 (t, *J* = 6.5 Hz, 4H), 1.87-1.99 (m, 4H), 1.65-1.56 (m, 4H), 1.44-1.35 (m, 8H), 1.09 (s, 18H), 1.07 (s, 18H), 0.95 (t, *J* = 6.3 Hz, 6H), 0.32 (s, 12H), 0.26 (12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 150.3, 146.6, 145.0, 124.1, 123.7, 123.3, 114.2, 113.9, 106.2, 68.8, 31.7, 29.5, 26.1, 25.8, 22.7, 18.5, 14.1, -4.1, -4.6 ppm.

General Deprotection Procedure: To a 0.1 M solution of TBDMS-protected triphenylene derivatives **10**, **21**, and **23** in 1:2 dimethylformamide:tetrahydrofuran was added potassium fluoride (8 equivalents), and aqueous hydrogen bromide (0.12 equivalents). The solution was stirred overnight with periodic monitoring by TLC. Aqueous potassium carbonate (1 M) was added, and the mixture stirred for an hour. The solution was slowly acidified with aqueous hydrochloric acid (1 M), and extracted with diethyl ether (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude material was purified by column chromatography, affording pure triphenylene tetra-ol derivatives **1**-**3**.

Compound 1: Reaction scale: TBDMS-protected triphenylene derivative **10** (245 mg, 0.258 mmol). The crude product was purified by column chromatography, eluting with ethyl acetate, to afford the pure product as a lavender solid (101 mg, 79%). Mp = >200 °C. ESI/APCI (m/z) $[MH]^+$ calculated for $C_{30}H_{37}O_6$, 493.2585: found 493.2575. ^1H NMR (300 MHz, acetone-d): δ 8.35 (s, 2H) 8.17 (s, 2H) 7.94 (s, 2H), 7.87 (s, 2H), 7.85 (s, 2H), 4.25 (t, *J* = 6.5 Hz, 4H), 1.84 - 1.96 (m, 4H), 1.55-1.67 (m, 4H), 1.34-1.48 (m, 8H), 0.91-0.98 (m, 6H) ppm. ^{13}C NMR (acetone-d6, 75 MHz): 149.7, 146.1, 124.2, 123.9, 109.1, 108.8, 108.7, 69.7, 32.5, 30.5, 26.7, 23.4, 14.4 ppm.

Compound 2: Reaction Scale: TBDMS-protected triphenylene derivative **21** (70 mg, 0.074 mmol). The crude product, while isolated as a relatively pure solid, was further purified by column chromatography eluting with 100% diethyl ether to obtain a pale orange solid (33 mg, 92%). Mp = 157 °C. ESI/APCI (m/z) $[MH]^+$ calculated for $C_{30}H_{37}O_6$, 493.2585: found 493.2583. ^1H NMR (300 MHz, acetone-d): δ 8.26 (s, 2H), 7.99 (s, 2H), 7.89 (s, 2H), 7.83 (s, 2H), 7.79 (s, 2H), 4.28 (t, *J* = 6.5 Hz, 4H), 1.84-1.93 (m,

4H), 1.50-1.62 (m, 4H), 1.32-1.44 (m, 8H), 0.92 (t, *J* = 6.2 Hz, 6H) ppm. ^{13}C NMR (acetone-d6, 75 MHz): 147.9, 147.2, 146.0, 124.4, 124.2, 123.7, 109.0, 108.7, 105.9, 69.6, 32.5, 30.4, 26.6, 23.4, 14.4 ppm.

Compound 3: Reaction Scale: TBDMS-protected triphenylene derivative **23** (140 mg, 0.147 mmol). The crude product, while isolated as a relatively pure solid, was further purified by column chromatography eluting with 100% diethyl ether to give a violet solid (38 mg, 52%). Mp = 130 °C. ESI/APCI (m/z) $[MH]^+$ calculated for $C_{30}H_{37}O_6$, 493.2585: found 493.2584. ^{1}H NMR (300 MHz, acetone-d6): δ 8.18 (s, 2H), 7.95 (s, 2H), 7.88 (s, 2H), 7.87 (s, 2H), 7.80 (s, 2H), 4.31 (t, *J* = 6.4 Hz, 4H), 1.85-1.96 (m, 4H), 1.51-1.64 (m, 4H), 1.32-1.45 (m, 8H), 0.93 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (acetone-d, 75 MHz): 147.5, 147.0, 146.0, 124.4, 123.8, 123.4, 108.7, 108.6, 106.1, 69.5, 32.4, 26.4, 23.1, 14.2 ppm.

Method B: To a 0.01 M solution of *ortho*-terphenyl derivatives **9**, **20**, and **22** in dry dichloromethane was added neat trifluoroacetic acid (10% with respect to volume of solvent), and the solution stirred for 30 minutes at room temperature. Oxidant DDQ (1.1 equivalents) was added at 0 °C, and the solution allowed to return slowly to room temperature over 3 hours. Water was added slowly, and the intermediate extracted with dichloromethane (3x). The combined organic layers were washed with saturated sodium bicarbonate (3x) and brine, dried over $MgSO_4$, and concentrated in vacuo. To a 0.1 M solution of the resulting residue in 1:1 dimethylformamide:tetrahydrofuran was added potassium fluoride (8 equivalents), and aqueous hydrogen bromide (0.12 equivalents). The solution was stirred overnight. Aqueous potassium carbonate (1 M) was added, and the mixture stirred for one hour. The solution was slowly acidified with aqueous hydrochloric acid (1 M), and extracted with diethyl ether (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude material was purified by column chromatography, or by recrystallization in ether:hexanes, affording pure triphenylene tetra-ol derivatives **1**-**3**

Compound 1: Reaction Scale: *ortho*-terphenyl **9** (500 mg, 0.525 mmol). The pure product was isolated by recrystallization from diethyl ether and hexanes (171 mg, 66%). This reaction has also been run at larger scales up to 2.8 grams of *ortho*-terphenyl **9**, giving tetraol **1** in similar yields. Characterization matched the data provided for compound **1** as synthesized using the two-step procedure (Method A).

Compound 2: Reaction Scale: *ortho*-terphenyl **20** (848 mg, 0.891 mmol). The pure product was isolated by column chromatography eluting with 10% acetone in dichloromethane (332 mg, 76%). Characterization matched the data provided for compound **2** as synthesized using the two-step procedure (Method A).

Compound 3: Reaction Scale: *ortho*-terphenyl **22** (718 mg, 0.754 mmol). The pure product was isolated by column chromatography eluting with 10% acetone in dichloromethane (251 mg, 67%). Characterization matched the data provided for compound **3** as synthesized using the two-step procedure (Method A).

General procedure for the preparation of amphiphilic triphenylenes: To a 0.1 M solution of triphenylene tetra-ol in dimethylformamide, was added 2-(2-methoxy-ethoxy)-ethyl-toluenesulphonate[33] (6 equivalents), potassium carbonate (8 equivalents), catalytic lithium bromide, and 18-crown-6 under inert conditions. The system was purged with nitrogen again, and the reaction stirred at 80 °C overnight. The solution was allowed to cool, water was added, and the crude product was extracted with diethyl ether (3x). The combined ethereal extracts were washed with aqueous hydrochloric acid (1M) and brine, and the combined aqueous layers back-extracted again with ether. The combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography, eluting with 10% acetone in dichloromethane.

Compound 4: Reaction scale: Compound **1** (65 mg, 0.132 mmol). Pure product was isolated as a brown oil that gradually solidified (70 mg, 59%). Mp = 37 °C. ESI/APCI (m/z) $[MNa]^+$ calculated for $C_{50}H_{76}O_{14}Na$, 923.5127: found 923.5148. ^1H NMR (300 MHz, CDCl3): δ 7.91 (s, 2H), 7.89 (s, 2H),

7.82 (s, 2H), 4.40-4.44 (m, 8H), 4.23 (t, *J* = 6.5 Hz, 4H), 3.98-4.02 (m, 8H), 3.78-3.83 (m, 8H), 3.60-3.63 (m, 8H), 3.42 (s, 12H), 1.90-2.00 (m, 4H), 1.55-1.61 (m, 4H), 1.37-1.45 (m, 8H), 0.94 (t, *J* = 6.6 Hz, 6H) ppm. ^{13}C NMR (CDCl3, 75 MHz): 149.1, 148.5, 124.0, 123.8, 123.4, 108.2, 107.8, 106.9, 71.9, 70.7, 69.9, 69.8, 69.5, 69.1, 69.0, 59.0, 31.6, 29.4, 25.8, 22.6, 14.0 ppm.

Compound 5: Reaction scale: Compound **2** (121 mg, 0.246 mmol). Pure product was isolated as a brown oil (132 mg, 60%). ESI/APCI (m/z) $[MNa]^+$ calculated for $C_{50}H_{76}O_{14}Na$, 923.5127: found 923.5137. ^{1}H NMR (300 MHz, CDCl3): δ 7.95-7.88 (m, 4H), 7.83 (s, 2H), 4.42 (t, *J* = 4.9 Hz, 8H), 4.23 (t, *J* = 6.5 Hz, 4H), 3.98-4.04 (m, 8H), 3.79-3.85 (m, 8H), 3.59-3.65 (m, 8H), 3.41 (s, 12H), 1.89-1.98 (m, 4H), 1.53-1.62 (m, 4H), 1.37-1.45 (m, 8H), 0.95 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (CDCl3, 75 MHz): 149.5, 149.0, 145.9, 124.3, 123.9, 108.3, 107.6, 72.02, 70.88, 70.80, 69.88, 69.56, 69.30, 69.15, 59.08, 31.67, 29.39, 25.82, 22.64, 14.04 ppm.

Compound 6: Reaction scale: Compound **3** (93 mg, 0.189 mmol). Pure product was isolated as a brown oil that gradually solidified (97 mg, 57%). Mp = 33 °C. ESI/APCI (m/z) $[MNa]^+$ calculated for $C_{50}H_{76}O_{14}Na$, 923.5127: found 923.5153. ^{1}H NMR (300 MHz, CDCl3): δ 7.90 (s, 2H) 7.88 (s, 2H) 7.82 (s, 2H), 4.42 (t, *J* = 4.2 Hz, 8H), 4.22 (t, *J* = 6.5 Hz, 4H), 3.88-4.03 (m, 8H), 3.78-3.84 (m, 8H), 3.59-3.63 (m, 8H), 3.41 (s, 12H), 1.89-2.00 (m, 4H), 1.53-1.64 (m, 4H), 1.34-1.46 (m, 8H), 0.94 (t, *J* = 6.6Hz, 6H) ppm. ^{13}C NMR (CDCl3, 75 MHz): 149.0, 148.5, 124.0, 123.7, 123.4, 108.3, 107.3, 106.7, 72.0, 71.9, 70.8, 69.9, 69.8, 69.4, 69.3, 69.1, 59.0, 31.6, 29.4, 25.8, 22.6, 14.0 ppm.

Spectroscopic Characterization

The key step in our synthesis of triphenylene tetra-ols **1**-**3** is the oxidative annulation of *ortho*-terphenyl derivatives to their corresponding triphenylene derivatives by DDQ in the presence of acid (TFA). This transformation is easily observed by ^{1}H NMR spectroscopy as diagnostic proton signals in

the aromatic region of the spectra of *ortho*-terphenyl compounds **9**, **20**, and **22** shift substantially downfield upon annulation to triphenylene derivatives **10**, **21**, and **23**, respectively. Figure 2 provides a representative example of these spectral changes highlighting the spectroscopic shifts observed upon annulation of *ortho*-terphenyl **9** to triphenylene **10**. Singlet H_a of the dihexyloxy ring shifts downfield from 6.85 ppm in *ortho*-terphenyl derivative **9** to 7.74 ppm in triphenylene derivative **10**. Proton signals H_b and H_c of the di(*tert*-butyldimethylsilyloxyl) rings, which overlap in the region from 6.60-6.67 ppm in **9**, separate into two distinct singlets at 7.79 and 7.83 ppm in annulated product **10**. Lastly, the doublet at 6.54 ppm that corresponds to proton H_d of *ortho*-terphenyl derivative **9** is no longer present in the annulated triphenylene derivative. Accurate mass APCI mass spectrometric analysis further supports the loss of two hydrogen atoms upon annulation: m/z = 951.6180 $[M+H]^+$ for *ortho*-terphenyl **9** and 949.6027 $[M+H]^+$ for triphenylene **10** ($\Delta m/z_{\mathbf{9\text{-}10}}$ = 2.0153) compared with calculated values of 951.6200 and 949.6044 ($\Delta m/z$ = 2.0156), respectively. Cleavage of the four TBDMS protecting groups of triphenylene derivative **10** with KF and HBr (Scheme 3) is accompanied by the loss of peaks at 0.98, 0.94, 0.19 and 0.08 ppm as well as a significant change in compound solubility: the deprotected triphenylene tetra-ol **1** displays very limited solubility in chloroform but is well solvated in more polar solvents such as acetone and tetrahydrofuran. Accurate mass APCI mass spectrometric analysis of triphenylene tetra-ol **1** reveals an $[M+H]^+$ signal at m/z = 493.2575, which is in agreement with the calculated value of 493.2585 and commensurate with the loss of four TBDMS groups. Similar changes in the ^{1}H NMR spectra and APCI mass spectra accompany the oxidative annulation and KF deprotection of *ortho*-terphenyl **20** to TBDMS-protected triphenylene **21** and ultimately tetra-ol **2**, as well as from regioisomeric *ortho*-terphenyl **22** to TBDMS-protected triphenylene **23** and tetra-ol **3**.

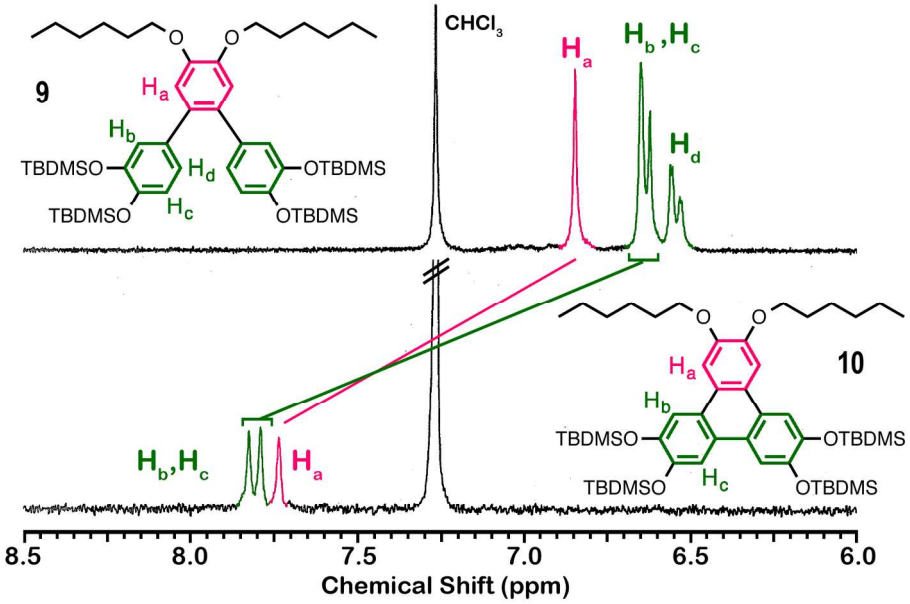


Figure 2. Representative partial ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of *ortho*-terphenyl derivative **9** (top) and TBDMS-protected triphenylene derivative **10** (bottom) indicating characteristic shifts of aromatic signals upon oxidative annulation.

While proton signals in the ^{1}H NMR spectra of **10**, **21**, and **23** support the successful formation of triphenylene derivatives, the three regioisomers cannot be distinguished by proton spectra alone. Similarly, mass spectroscopic analyses of the three TBDMS-protected triphenylene derivatives are, within error, identical (*m/z* = 946.6027, 949.6031, and 949.6034 $[M+H]^+$ for **10**, **21**, and **23**, respectively). ^{13}C NMR spectroscopy, however, does provide a means of distinguishing between the three different isomers. As shown in Figure 3, the nine carbon signals in the aromatic region of **10**, **21**, and **23** can be grouped into three clusters of three peaks each. The quaternary carbons of the central six-member ring of each triphenylene, labeled C_1-C_3 in Figure 3, are the farthest downfield (144-150 ppm) due to greater deshielding in this central ring. The peripheral quaternary carbon atoms (C_4-C_6 in Figure 3) fall within a tighter range of 123-125 ppm. Lastly, the methine carbons (C_7-C_9 in Figure 3) are found between 106-114 ppm.

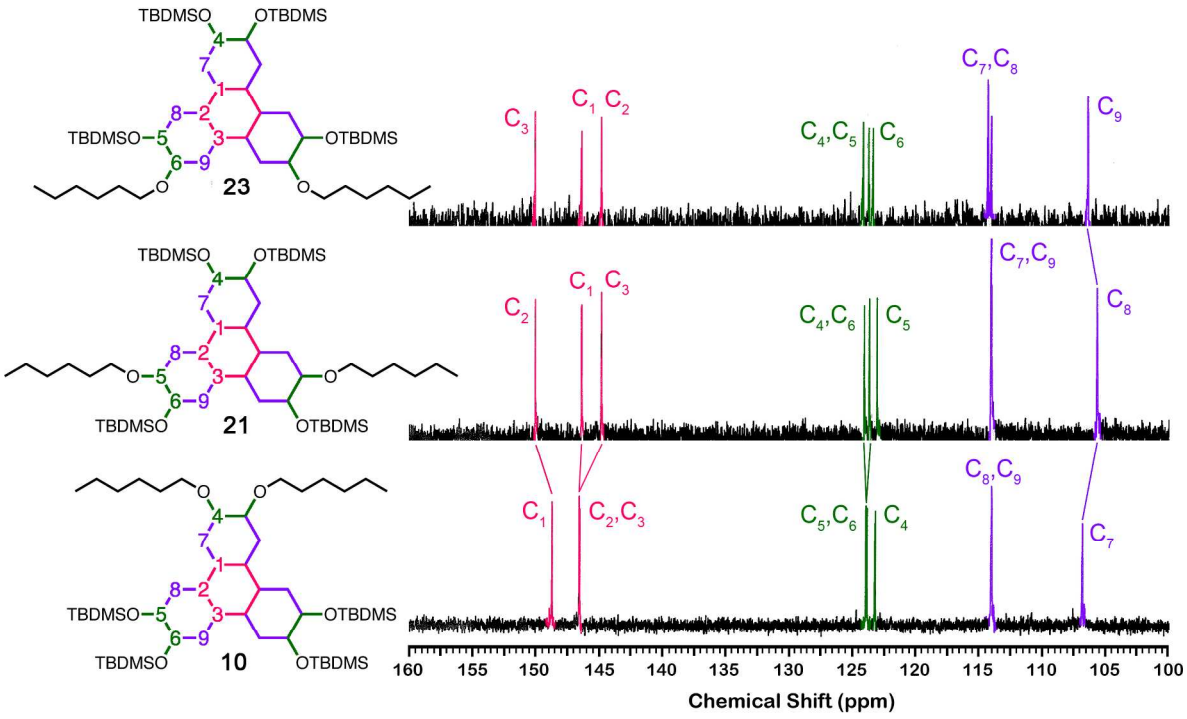


Figure 3. Partial ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of TBDMS-protected triphenylene derivatives **23** (top), **21** (middle), and **10** (bottom) highlighting the differences in chemical shift that distinguish each regioisomer.

As can be seen in Figure 3, the carbon signals C_1-C_3 of triphenylene derivatives **21** and **23** are highly similar while those of **10** are more distinct. This distinction comes from the fact that carbon C_1 of compound **10** at 148.7 ppm is contained within an aryl ring bearing two hexyloxy substituents, a feature not present in any of the aryl rings of isomers **21** or **23**. Furthermore, carbons C_2 and C_3 of compound **10** both appear at 146.6 ppm as they occupy almost identical positions within aryl rings bearing two OTBDMS groups. Three distinct signals are observed for carbon atoms C_1-C_3 of compounds **21** and **23**: one assigned to a carbon atom within a di(OTBDMS) ring, one assigned to a carbon atom proximal to the hexyloxy group of a mixed hexyloxy/OTBDMS ring, and one assigned to a carbon atom proximal to the OTBDMS group of a mixed hexyloxy/OTBDMS ring. Given this similarity between isomers **21** and **23** the signals for carbons C_1-C_3 appear almost indistinguishable.

In the middle cluster of signals, corresponding to carbon atoms C_4-C_6, isomer **10** again displays a distinct pattern while isomers **21** and **23** are significantly more similar. Carbon signals for compound **10** in this region appear at two chemical shifts: one isolated peak corresponding to C_4 at 123.2 ppm and two

overlapping peaks corresponding to carbon atoms C_5 and C_6 at 124.0 ppm. Carbon atom C_4 is distinct as it is substituted with hexyloxy groups whereas C_5 and C_6, while symmetrically inequivalent, are both substituted with an OTBDMS group and are observed at the same chemical shift. Isomers **21** and **23** again display three distinct peaks for C_4-C_6 following the same reasons as discussed above for distinguishing their C_1-C_3 signals. Lastly, isomers **21** and **23** can be distinguished from each other by the shifts of methine carbon signals in the region spanning 106-114 ppm. Within this region the carbon atom alpha to a hexyloxy-substituted peripheral carbon is found farthest upfield and at a unique chemical shift: 106.8 for C_7 of **10**, 105.8 for C_8 of **21**, and 106.2 for C_9 of **23**. Furthermore, in compound **23**, methine carbon atoms C_7 and C_8 are in subtly distinct chemical environments such that their signals appear close (114.2 and 113.9, respectively) but do not overlap. For isomers **10** and **21**, however, signals for the methine carbon atoms alpha to OTBDMS-substituted peripheral carbon atoms are sufficiently similar that they do overlap and cannot be resolved. Collectively, the nine aromatic carbon signals in the ^{13}C NMR spectra of triphenylene isomers **10**, **21**, and **23** provide a means of distinguishing each isomer.

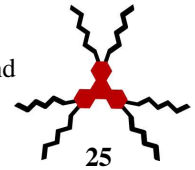
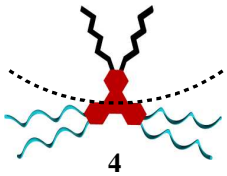
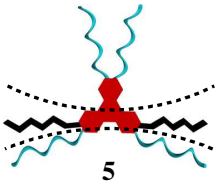
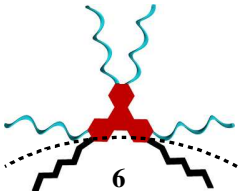
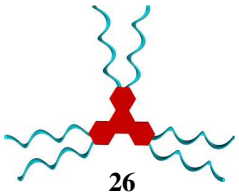
Functionalization of triphenylene tetra-ols **1**-**3** to give amphiphilic, mixed-substituent triphenylenes **4**-**6** was confirmed by the disappearance of hydroxyl peaks and concomitant appearance of ethylene glycol peaks in the region extending from 3.4 to 4.5 ppm of the ^{1}H NMR spectra of each species. Functionalization with monomethyl di(ethylene glycol) chains was also accompanied by a notable increase in the solubility of each compound and a phase change from high melting solid materials to low melting solids (**4** and **6**) and one liquid (**5**). Mass spectroscopic analysis confirmed the addition of four monomethyl di(ethylene glycol) substituents to compounds **1**-**3**, revealing $[M+Na]^+$ signals at *m/z* = 923.5148, 923.5137, and 923.5153 for mixed-substituent triphenylene derivatives **4**-**6**, respectively, compared to the calculated value of 923.5127. The three triphenylene tetra-ols **1**-**3** and amphiphilic triphenylenes **4**-**6** were also characterized by UV/Vis spectroscopy. Spectra of all six compounds display nearly identical absorption maxima (λ_{max} = 345±1 nm) with extinction coefficients ranging from ε = 3.2-4.9x10^4 M^{-1} cm^{-1} (see Figures S1 and S2 of the Supporting Information). These absorption characteristics closely mirror those of fully symmetric hexakis(hexyloxy) triphenylene (λ_{max} = 346

nm, ε = 5.2x10^4 M^{-1} cm^{-1}), hexa(hydroxy) triphenylene (λ_{max} = 346 nm, ε = 4.0x10^4 M^{-1} cm^{-1}), and hexakis(monomethyl di(ethylene glycol)) triphenylene (λ_{max} = 345 nm, ε = 4.0x10^4 M^{-1} cm^{-1}).

Lastly, the thermal properties of new amphiphilic triphenylene derivatives **4**-**6** were investigated by differential scanning calorimetry (DSC) and compared to symmetric control compounds hexakis(hexyloxy) triphenylene (**25**) and hexakis(monomethyl di(ethylene glycol)) triphenylene (**26**). As noted earlier, monomethyl di(ethylene glycol) substituents were chosen because ethylene glycol chains are less crystalline than comparable length alkyl chains. Indeed, DSC analysis of hexakis(hexyloxy) triphenylene **25** reveals a sharp crystallization at 51 °C whereas crystallization is supressed for hexakis(monomethyl di(ethylene glycol)) triphenylene **26** (Table 2 and Figures S3 and S4 of the Supporting Information). Furthermore, alkyl-substituted **25** exhibits a mesophase between 56 and 64 °C, in good agreement with the reported formation of a columnar hexagonal (Col_h) liquid crystalline phase.[35] Hexakis(monomethyl di(ethylene glycol))-substituted **26**, by contract, becomes isotropic at 47 °C with no evidence of mesophase formation. The thermal properties of amphiphilic triphenylenes **4**-**6** may be expected to vary between those of triphenylenes **25** and **26**, and provide a means of assessing the influence of alkyl versus ethylene glycol regiochemistry on triphenylene phase behavior.

Table 2. Phase transition temperatures (°C) of substituted triphenylenes. Transition temperatures are based on the 1st cooling run (5$^{°C}/_{min}$) and 2nd heating run (10$^{°C}/_{min}$). T_M = Transition to mesophase, T_I = clearing temperature (isotropic melt). In the schematic representations of compounds **4**-**6** and **25**-**26**,

hexyloxy substituents are represented by angular black lines and monomethyl di(ethylene glycol) substituents are represented by blue helices. Dashed lines indicate divisions between hydrophobic and hydrophilic sections of triphenylene derivatives **4**-**6**.

Compound	 **25**	 **4**	 **5**	 **6**	 **26**
T_M	56	37	-6	33	-
T_I	64	55	28	44	47
Mesophase	Col_h	Col_h	[a]	Col_h	-

[a] Compound 5 exhibits a broad mesophase between -6 and 28 °C. Dissimilarity from the characteristic columnar hexagonal mesophase prevents conclusive mesophase characterization other than a possible ordered nemetic phase.

Shown in Table 2 are the phase transitions of triphenylene derivatives **4**-**6** and **25**-**26**. Also shown in Table 2 are schematic representations of each triphenylene derivative that aid in understanding how substituent regiochemistry in amphiphilic triphenylenes influences thermal phase transitions. Of the three amphiphilic triphenylenes studied, compound **4**, bearing hexyloxy substituents at positions 2 and 3, was found to behave most similar to hexakis(hexyloxy) triphenylene **25**. Compound **4** shows a sharp crystallization at a lower temperature than all-hexyloxy **25** (39 °C versus 51°C) and similarly transitions to isotropic at a lower temperature than compound **25** (57 °C versus 64 °C), as would be expected with the introduction of monomethyl di(ethylene glycol) chains. It is interesting to note that amphiphilic triphenylene **4** exhibits a broader mesophase (37-57 °C) than all-hexyloxy triphenylene **25** (56-64 °C). By contrast, amphiphilic triphenylene derivative **5**, with hexyloxy substituents at the 2 and 7 positions, does not show a sharp melt (or crystallization) but rather a broad transition around -6 °C. A second transition is observed at 28 °C, likely indicating the formation of a nematic mesophase rather than a columnar phase more typical of compound **25**. Lastly, compound **6** with hexyloxy substituents at

positions 3 and 6 exhibits a narrower mesophase between 33 and 44 °C. Compound **6**, therefore, becomes isotropic at a temperature below triphenylene derivatives **4**, **25**, and **26** yet above derivative **5**. Similar to hexakis(monomethyl di(ethylene glycol)) triphenylene **25**, no distinct crystallization could be observed for amphiphilic triphenylene derivative **6**.

The results presented in Table 2 clearly show that the relative placement of hexyloxy chains in amphiphilic triphenylene derivatives **4**-**6** significantly influence their phase behavior. Given the observed results, we hypothesize that the primary factor influencing phase behavior in compounds **4**-**6** is the relative spacing of their two hexyloxy substituents. Alkyl chains are known to promote crystallinity and long-range order in triphenylene mesogens.[1-3] As such, placement of the two hexyloxy chains as close to each other as possible – i.e. 2,3-bis(hexyloxy) derivative **4** – results in the amphiphilic derivative with the highest clearing temperature of 57 °C along with a well-defined crystallization (see Figures S3 and S4 of the Supporting Information). The clearing temperature of the amphiphilic 2,6-bis(hexyloxy) derivative **6**, with its hexyloxy substituents spaced slightly further apart than in compound **4**, is observed 13 °C lower at 44 °C. Amphiphilic derivative **5** is notably different than derivatives **4** and **6** because its hexyloxy substituents are almost diametrically opposed at positions 2 and 7. As such, monomethyl di(ethylene glycol) substituents fully segregate the two hexyloxy substituents from each other (as indicated by dashed curves in Table 2) whereas hexyloxy substituents are not similarly segregated from each other in derivatives **4** and **6**. This greater separation of hexyloxy substituents further inhibits crystallization and depresses the clearing temperature of derivative **5** to 28 °C. Further investigation of mixed hexyloxy and monomethyl di(ethylene glycol) substituted triphenylenes that vary in both the stoichiometry (1:5 through 5:1) and relative positioning of the different substituents will be necessary to determine if this preliminary trend is more broadly applicable. Such investigations are currently underway.

Conclusion

The synthesis of hydroxy-functionalized triphenylene derivatives via oxidative annulation of *ortho*-terphenyl compounds is reliable, facile, scalable, and opens innumerable routes to the synthesis of structurally precise mixed-substituent triphenylene derivatives. In the current study, three isomers of rationally-designed tetrahydroxy triphenylene derivatives were synthesized. The good to excellent yields and straightforward purifications of the synthetic route presented herein offer a valuable alternative to the current harsh, non-selective methods that are typical of triphenylene poly-ol syntheses. The tetrahydroxy triphenylene derivatives provide a versatile platform for further synthetic modifications, as demonstrated here by their functionalization with monomethyl di(ethylene glycol) chains to provide three regioisomers of amphiphilic triphenylenes bearing two hexyloxy and four monomethyl di(ethylene glycol) substituents. Furthermore, the importance of regioisomerism on the physical properties of triphenylene mesogens was demonstrated in differences in the thermal properties of the three amphiphilic triphenylene isomers as compared to each other and to hexakis(hexyloxy) triphenylene and hexakis(monomethyl di(ethylene glycol)) triphenylene.

The adaptability of the synthetic routes presented herein is evident in the precursor design: functional groups and their regiochemistry may be easily varied by small changes in precursor substituent patterns. Similarly, multiple different functionalities can be introduced at several points in the synthesis, providing facile routes to mixed triphenylene derivatives with two – or more – types of substituents. The synthetic routes demonstrated herein can likely be adapted to the preparation of heterocyclic triphenylene derivatives such as azatriphenylenes,[36-39] which are known to exhibit different electronic and physical properties[36-37] than triphenylene derivatives but their development has been limited by the current use of toxic and costly transition metal catalysts in their synthesis.[38-39] In general, we anticipate triphenylene derivatives will continue to play vital roles in the development of multifunctional mesogens with implications in such areas as organic electronic and photovoltaic materials, and rational routes to multifunctional triphenylene derivatives, such as those described herein, will allow the full potential of these unique compounds to be explored and applied.

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Supporting Information Available: Full experimental procedures and spectroscopic characterization (^{1}H and ^{13}C NMR, mass, and UV/Vis spectra) of newly reported compounds and differential scanning calorimetry (DSC) traces of compounds **4**-**6** and **25**-**26**.

References

[1] a) S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 1977, **9**, 471. b) S. Chandrasekhar and G. S. Ranganath, *Rep. Prog. Phys.*, 1990, **53**, 57. c) *Handbook of Liquid Crystals – Low Molecular Weight Liquid Crystals, Vol. 2B*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley VCH, Weinheim, 1998. d) D. Demus, *Mol. Cryst. Liq. Cryst.*, 2001, **364**, 25. e) R. J. Bushby and O. R. Lozman, *Curr. Op. Colloid and Interface Sci*., 2002, **7**, 343. f) S. Kumar, *Liq. Cryst.*, 2005, **32**, 1089.

[2] a) S. Kumar, *Liq. Cryst.*, 2004, **31**, 1037. b) S.K. Pal, S. Setia, B. S. Avinash and S. Kumar, *Liq. Cryst.*, 2013, **40**, 1769.

[3] a) M. Watson, A. Fechtenkötter and K. Müllen, *Chem. Rev.*, 2001, **101**, 1267. b) D. Perez and E Guitián, *Chem. Soc. Rev*., 2003, **33**, 274.

[4] a) S. Kumar, *Liq. Cryst*., 2005, **32**, 1089. b) B. Kaafarani, *Chem. Mater.*, 2011, **23**, 378.

[5] a) R. J. Bushby and O. R. Lozman, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 569. b) K. Senthilkumar, F. C. Grozema, F. M. Bickelhaupt and L. D. A. Siebbeles, *J. Chem. Phys*., 2003, **119**, 9809. c) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, *Angew. Chem. Int. Ed.*, 2007, **46**, 4832.

[6] a) A. Bacher, I. Bleyl, C. H. Erdelen, D. Haarer, W. Paulus and H. W. Schmidt, *Adv. Mater.*, 1997, **9**, 1031. b) I. H. Stapff, V. Stümpflun, J. H. Wendorff, D. B. Spohn and D. Mobius, *Liq. Cryst.*, 1997, **23**, 613. c) T. Christ, B. Glüsen, A. Greiner, A. Kettner, R. Sander, V. Stümpflun, V. Tsukruk and J. Wendorff, *Adv. Mater.*, 1997, **9**, 48. d) I. Seguy, P. Destruel and H. Bock, *Synth. Met.*, 2000, **111**, 15. e) S. A. Benning, T. Hasseider, S. Keuker-Baumann, H. Bock, F. Della Sala, T. Frauenheim, H. S. Kitzerow, *Liq. Cryst*. 2001, **28**, 1105.

[7] a) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Nature*, 1994, **371**, 141. b) N. Boden, R. J. Bushby, A. N. Cammidge, J. Clements and R. Luo, *Mol. Cryst. Liq. Cryst.*, 1995, **261**, 251. c) V. S. K. Balagurusamy, S. K. Prasad, S. Chandrasekhar, S. Kumar, M. Manickam and C. V. Yelamaggad, *Pramana*, 1999, **53**, 3. d) K. Ohta, K. Hatsusaka, M. Sugibayashi, M. Ariyoshi, K. Ban, F. Maeda, R. Naito, K. Nishizawa, A. van de Craats, *Mol. Cryst. Liq. Cryst.*, 2003, **397**, 25.

[8] C. F. Van Nostrum, *Adv. Mater.*, 2004, **8**, 1027.

[9] K. Praefcke and A. Eckert, *Mol. Cryst. Liq. Cryst.*, 2003, **396**, 265.

[10] a) S. Kumar, *Chem. Soc. Rev.*, 2006, **35**, 83. b) N. Boden, R. C. Borner, R. J. Bushby, A.N. Cammidge and M. V. Jesudason, *Liq. Cryst.*, 2006, **33**, 1443

[11] a) G. Heppke, D. Kruerke, C. Lohning, D. Lotzsch, D. Moro, M. Muller and H. Sawade, *J. Mater. Chem.*, 2000, **10**, 2657. b) L. H. Wu, N. Janarthanan, C. S. Hsu. 2001. *Liq. Cryst.*, **28**, 17. c) J. Barbera, A. C. Garces, N. Jayaraman, A. Omenat, J. L. Serrano and J. F. Stoddart, *Adv. Mater.*, 2002, **13**, 175.

[12] A. N. Cammidge and H. Gopee, *J. Mater. Chem.*, 2001, **11**, 2773.

[13] a) C. T. Imrie, Z. Lu, S. J. Picken and Z. Yildirim, *Chem Commun.,* 2007, 1245. b) V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, R. Graf, H. W. Spiess, V. S. K. Balagurusamy and P. A. Heiney, *J. Am Chem. Soc.*, 2009, **131**, 7662.

[14] a) E. O. Arikainen, N. Boden, R. J. Bushby, J. Clements, B. Movaghar and A. Wood, *J. Mater. Chem.*, 1995, **5**, 2161. b) V. Lemaur, D.A. Silva Filho, V. Coropceanu, M. Lehmann, Y. Geerts., J. Piris, M. G. Debije, A. N. van de Craats, K. Senthilkumar, L. D. A. Siebbeles, J. M. Warman, J-L. Brédas and J. Cornil, *J. Am. Chem. Soc.*, 2004, **126**, 3271.

[15] O. C. Musgrave, *Chem. Rev.*, 1969, **69**, 499.

[16] a) R. C. Borner and R. F. W. Jackson, *J. Chem. Soc., Chem. Commun.*, 1994, **7**, 845. b) R. Freudenmann, B. Behnisch and M. Hanack, *J. Mater. Chem.*, 2001, **11**, 1618. c) D. Simoni, G. Giannini, P. G. Baraldi, R. Romagnoli, M. Roberti, R. Rondanin, R. Baruchello, G. Grisolia, M. Rossi, D. Mirizzi, F. P. Invidiata, S. Grimaudo and M. Tolomeo, *Tetrahedron Lett.,* 2003, **44**, 3005.

[17] a) N. Boden, R. J. Bushby and A. N. Cammidge, *J. Chem. Soc., Chem. Commun.*, 1994, **4**, 465. b) O. Sarhan and C. Bolm, *Chem. Soc. Rev.*, 2009, **38**, 2730.

[18] S. Kumar and M. Manickam, *Chem Commun.*, 1997, **17**, 1615.

[19] a) N. Boden, R. J. Bushby and A. N. Cammidge, *J. Am. Chem. Soc.*, 1995, **117**, 924. b) P. Henderson, H. Ringsdorf and P. Schuhmacher, *Liq. Cryst.*, 1995, **18**, 191. c) R. Abeysekera, R. J. Bushby, C. Caillet, I. W. Hamley, O. R. Lozman, Z. Lu and A. W. Robards, *Macromolecules*, 2003, **36**, 1526. d) H. Wu, C. Zhang, J. Pu and Y. Wang, *Liq. Cryst.*, 2014, **41**, 1173

[20] W. Kreuder and H. Ringsdorf, *Makromol. Chem. Rapid Commun.*, 1983, **4**, 807.

[21] R. J. Bushby and Z. B. Lu, *Synthesis*, 2001, 763

[22] S. Kumar and M. Manickam. *Synthesis.*, 1998, 1119.

[23] a) X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.*, 2012, **41**, 6010. b) S-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548. c) J. W. Colson and W. R. Dichtel, *Nat. Chem.*, 2013, **5**, 453.

[24] M. K. Smith, N. E. Powers-Riggs, and B. H. Northrop, *Chem. Commun* 2013, **49**, 6167.

[25] A. P. Côte, A. I. Benin, N. W. Ockwig, M. O´Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1160.

[26] a) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147. b) A. Suzuki, *Angew. Chem. Int. Ed.* 2011, **50**, 6722.

[27] a) V. Bhalla, H. Singh and M. Kumar, *Org. Lett.*, 2010, **12**, 628. b) V. Bhalla, A. Gupta, Roopa, H. Singh and M. Kumar, *J. Org. Chem.* 2011, **76**, 1578. c) V. Bhalla, H. Singh, H. Arora and M. Kumar, *Sensor Actuat. B-Chem.* 2012, **171**, 1007.

[28] a) L. Zhai, R. Shukla and R. Rathore, *Org. Lett.*, 2009, **11**, 3474. b) L. Zhai, R. Shukla, S. H. Wadumethridge, R. Rathore, *J. Org. Chem.* 2010, **75**, 4748. c) T. S. Navale, K. Thakur, R. Rathore, *Org. Lett.*, 2011, **13**, 1634.

[29] E. Font-Sanchis, F. J. Cespedes-Guirao, A. Sastre-Santos, B. Villacampa, J. Orduna, R. Alicante and F. Fernandez-Lazaro, *Tetrahedron*, 2009, **65**, 4513

[30] K. L. Billingsley and S. L. Buchwald, *J. Org. Chem.*, 2008, **73**, 5589.

[31] Q. Peng, Z-Y. Lu, Y. Huang, M-G. Xie, S-H. Han, J-B. Peng and Y. Cao, *Macromolecules*, 2004, **37**, 260.

[32] M. Van der May, A. Hatzelmann, G. P. M. Van Klink, I. J. Van der Laan, G. J. Sterk, U. Thibaut, W. R. Ulrich and H. Timmerman, *J. Med. Chem.*, 2001, **44**, 2523.

[33] The only reaction reported herein that proceeds in a low yield is the mono-alkylation of catechol to form compound **11** (30% yield). We do not envision this to be a prohibitive problem given that

catechol and hexyl bromide are both readily available and inexpensive. Furthermore, this single low yielding reaction is the first step in a synthetic sequence, which helps negate product loss.

[34] J. R. Harjani, C. Liang, P. G. Jessop, *J. Org. Chem.* 2011, **76**, 1683.

[35] J. Schulte, S. Laschat, R. Schulte-Ladbeck, V. von Arnim, A. Schneider and H. Finkelmann, *J. Organomet. Chem.*, 1998, **552**, 171.

[36] M. Palma, J. Levin, V. Lemaur, A. Liscio, V. Palermo, J. Cornil, Y. Geerts, M. Lehmann, P. Samori *Adv. Mater.* 2006, **18**, 3313.

[37] M. Palma, J. Levin, O. Debever, Y. Geerts, M. Lehmann, P. Samori *Soft Matter* 2008, **4**, 303.

[38] A. McIver, D. D. Young, A. Deiters *Chem. Commun*. 2008, 4750.

[39] K. Murayama, Y. Sawada, K. Moguchi, K. Tanaka *J. Org. Chem.* 2013, **78**, 6202.

Table of Contents Entry

The synthesis of three new tetra(hydroxy)-triphenylene derivatives and their use as platforms for rationally designed, mixed-substituent triphenylene derivatives is described.