2.1. Introduction

Triphenylene derivatives have great potential in supramolecular and material chemistry owing to their role as liquid crystalline materials, molecular scale devices, and molecular receptors. Particularly appealing are hexasubstituted derivatives as peripheral substitution on triphenylene core has a large effect on the thermal behaviour of liquid crystalline materials. Triphenylene as a core for discotic liquid crystals (DLCs) is attractive for many reasons: (i) it possesses C$_3$ symmetry, (ii) its chemistry is relatively accessible, (iii) its derivatives are thermally as well as chemically stable and (iv) they show a variety of mesophases. However, the only existing rational routes for the synthesis of symmetrically/unsymmetrically hexasubstituted triphenylenes involve the iodine promoted photo-cyclization\(^9\) (Scheme 2.1A) or iron(III) chloride\(^10\) promoted oxidative cyclization (Scheme 2.1B) of ortho-terphenyls which are prepared by Ullman coupling reaction or by palladium catalyzed cross coupling reactions involving aryl boronic acid (Scheme 2.1C). Iron(III) chloride and MoCl$_5$\(^11\) have been shown to promote the cyclotrimerization of 1,2-dialkoxybenzene derivatives and also to allow a selective coupling of a 3,3',4,4'-tetraalkoxybiphenyl and a 1,2-dialkoxybenzene.\(^12\) Both photochemical and oxidative cyclization methods have their own limitations. For example, photo-cyclization method is efficient for the synthesis of symmetrically substituted triphenylenes but unsymmetrical substitution introduces the problem of regioselectivity and hence decreases the yield.

**Photochemical cyclization**

![Scheme 2.1A](image)

**Oxidative cyclization**

![Scheme 2.1B](image)

Scheme 2.1: Synthesis of triphenylene from terphenyl

Oxidative methods involve cyclization using the various oxidizing reagents and all of these reagents, iron(III) chloride and molybdenum chloride are insoluble in common organic
solvents, therefore, the synthesis of triphenylenes from terphenyls on a large scale using these conventional oxidizing agents is inconvenient.

![Scheme 2.1C: Synthesis of terphenyl by Pd-catalyzed Suzuki-Miyaura cross coupling](image)

Keeping in view the importance of triphenylenes and limitations of conventional cyclization methods, the development of new methods which allow the preparation of triphenylenes on large scale without using oxidizing reagents will be very beneficial. In the present chapter, we have developed a simple strategy for the preparation of triphenylene derivatives. For this purpose, we designed and synthesized various terphenyl derivatives having tert-butyldimethylsilyloxy (-OTBS) groups using Suzuki-Miyaura cross coupling. During the deprotection of –OTBS groups in the presence of tetrabutylammonium fluoride (TBAF), some of these derivatives undergo the fluoride-induced cyclization smoothly without using any oxidizing agents to give symmetrically and unsymmetrically substituted triphenylene derivatives.

Further, these derivatives also act as chromogenic and fluorogenic chemodosimeters for the fluoride ions which play an important role in broad range of chemical and biological processes\(^1\), for example, prevention of dental caries\(^2\) and in the treatment of osteoporosis\(^3\). However, high concentration\(^4\) of F\(^-\) ions can affect essential cellular components and cellular metabolism. Fluoride ions are also associated with anaesthetics, hypnotics, psychiatric drugs, nerve gases, in the analysis of drinking water and in the refinement of uranium used in nuclear weapon manufacture\(^5\). Therefore, the development of sensitive receptors for the detection of fluoride ions has attracted great attention. These are of two types of receptors, chemosensor and chemodosimeter. If the specific interaction between the host and the guest is noncovalent and reversible which can be disrupted under certain conditions, the receptor is referred as chemosensor (Figure 2.1a). However, in case of chemodosimeter the binding interaction between the host and the guest is based on an irreversible chemical reaction (Figure 2.1b). Most of the reported fluoride ion chemosensors are based upon the hydrogen bonding or Lewis acid coordination\(^6\) They suffer from serious limitation that they can sense fluoride ions only in high concentration and hence not highly selective. On the other hand, reaction based receptors i.e. chemodosimeters (Figure 2.1b) exhibit high selectivity and sensitivity\(^7\). However, most of the reported chemodosimeters\(^8\) require longer time for the
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

detection process whereas the response of chemodosimeters being reported in this chapter towards the fluoride ions is very fast.

![Diagram](image)

**Figure 2.1.** Schematic representation of (a) chemosensor and (b) chemodosimeter.

For the convenience in presentation, this chapter has been divided into following three sections which are discussed as follows.

1. **Synthesis of symmetrically and unsymmetrically substituted triphenylene derivatives**
2. **Synthesis of unsymmetrically substituted triphenylene derivatives having crown moieties**
3. **Synthesis of symmetrically substituted extended triphenylene derivatives**

### 2.2. Results and discussion

#### 2.2.1. Synthesis of symmetrically and unsymmetrically substituted triphenylene derivatives

We synthesized a number of symmetrically and unsymmetrically substituted terphenyl derivatives 14, 15 and 21 having –OTBS groups by using Suzuki-Miyaura cross coupling. Out of these, terphenyl derivatives 14 and 15 undergo facile cyclization to give triphenylene derivatives 17a and 17b respectively, during the de-protection of –OTBS groups in the presence of tetrabutylammonium fluoride (TBAF). Further, both these derivatives also act as chemodosimeters for the fluoride ions. The results of synthesis of various derivatives are discussed below:

The bromination of catechol 1 with Br₂ in carbon tetrachloride (CCl₄) gave dibromo derivative 2 in 86% yield (Scheme 2.2). Alkylation of 2 with tert-butyldimethylsilylchloride (TBDMSCI) in the presence of imidazole as base gave compound 3 in 94% yield. Likewise alkylation of 2 with methyl iodide in the presence of K₂CO₃ as base gave compound 4 in 91% yield. The deprotection of 4-bromoveratrole 5 with BBr₃ in dry CH₂Cl₂ at -78°C gave
compound 6 in 86% yield. Reaction of compound 6 with TBDMSCl in dry DMF gave alkylated compound 7 in 60% yield.

The boronic ester 9 was prepared in 57% yield by carrying out reaction of bromo derivative 7 with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8 in the presence of PdCl$_2$(PPh$_3$)$_2$ as catalyst (Scheme 2.3). The $^1$H NMR spectrum of compound 9 showed two singlets (12H, 18H) at 0.19 and 0.98 ppm due to the protons of tert-butyldimethylsilyl group, one singlet (12H) at 1.31 ppm due to the methyl groups and one multiplet (3H) at 7.03-7.10 ppm due to the aromatic protons.

Similarly, the boronic ester 10 was synthesized in 55% yield by carrying out the reaction of 4-bromoveratrole 5 with the 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8 (Scheme 2.4). The $^1$H
NMR spectrum of compound 10 showed one singlet (12H) at 1.34 ppm corresponding to the methyl protons, two singlets (3H, each) at 3.90 and 3.92 ppm due to the methoxy groups, one singlet and two doublets (1H, each) at 6.88, 7.28 and 7.42 ppm due to the aromatic protons. The compounds 12a (89%) and 12b (92%) were synthesized in a similar fashion by the alkylation of 3-bromophenol 11a and 4-bromophenol 11b, respectively, with TBDMSI in the presence of imidazole. The Pd(II)-catalyzed reaction of 12a and 12b with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8 gave corresponding boronic esters 13a and 13b in 62% and 67% yield, respectively (Scheme 2.5). The $^1$H NMR spectrum of compound 13a showed two singlets (6H, 9H) at 0.02 and 0.99 ppm due to tert-butyldimethylsilyleoxy group, one singlet (12H) at 1.26 ppm due to the methyl groups, one singlet, one doublet and one multiplet (1H, 1H, 2H) at 6.85, 6.95 and 7.29-7.32 ppm due to the aromatic protons. Similarly, the $^1$H NMR spectrum of compound 13b showed two singlets (6H, 9H) at 0.02 and 0.78 ppm due to tert-butyldimethylsilyleoxy group, one singlet (12H) at 1.13 ppm due to the methyl groups and two doublets (2H, each) at 6.64 and 7.50 ppm due to the aromatic protons.

Palladium(0) catalyzed Suzuki-Miyaura cross coupling of boronic ester 9 with dibromo derivatives 3 and 4 furnished terphenyls 14 and 15 in 86% and 79% yields, respectively (Scheme 2.6). The structures of compounds 14 and 15 were confirmed from their spectroscopic and analytical data. The $^1$H NMR spectrum of compound 14 showed six singlets (12H, 12H, 12H, 18H, 18H, 18H) at 0.12, 0.13, 0.18, 0.96, 0.98 and 1.02 ppm for protons of tert-butyldimethylsilyleoxy groups, three doublets and one singlet (2H, each) at 6.42, 6.58, 6.68 and 6.79 ppm due to the aromatic protons of terphenyl moiety. The FAB mass spectrum showed a parent ion peak at 1011 (M)$^+$ corresponding to coupled product 14. The $^1$H NMR spectrum of 15 in CDCl$_3$ showed four singlets (12H, 12H, 18H, 18H) at 0.07, 0.18, 0.93 and 0.98 ppm due to the tert-butyldimethylsilyleoxy groups, one singlet (6H) at 3.92 ppm due to the methoxy groups, one doublet, one multiplet and one singlet (2H, 4H, 2H) at 6.56,
6.63-6.66 and 6.84 ppm due to the aromatic protons of terphenyl moiety. The ESI mass spectrum showed a parent ion peak at 811 (M)$^+$ corresponding to coupled product 15. These spectroscopic data corroborate the structure 14 and 15 for these compounds. In the next step, we carried out the deprotection of terphenyls 14 and 15 using tetrabutylammonium fluoride (TBAF). Interestingly, the treatment of terphenyl 14 with TBAF furnished hexahydroxy triphenylene 17a in 93% yield along with drastic color changes from colourless to dark violet. The deprotection reaction was complete in five minutes and probably it involved two steps. The first step is cleavage of Si-O bond in the presence of F$^-$ ion followed by cyclization and both steps are very fast and irreversible.

The structure of compound 17a was confirmed from its spectroscopic data. The $^1$H NMR spectrum of compound 17a showed one singlet (6H) at 7.58 ppm for protons of triphenylene core. Similarly, de-protection of 15 with TBAF yielded compound 17b in 91% yield. The $^1$H NMR spectrum of 17b in THF-$d_8$ showed one singlet (6H) at 3.97 ppm due to methoxy...
groups, five singlets (2H, each) at 7.70, 7.77, 7.79, 8.10 and 8.25 ppm due to triphenylene core and hydroxyl groups. Compounds 17a and 17b were further confirmed by their conversion to derivatives 18 and 19 in 65% and 68% yield respectively. The $^1$H NMR spectrum of 18 showed a singlet (6H) at 8.56 ppm due to triphenylene core and that of 19 showed a singlet (6H) at 4.17 ppm due to the methoxy groups and three singlets (2H, each) at 7.76, 8.47 and 8.52 ppm due to triphenylene core. The FAB mass spectra showed parent ion peaks at 1116 (M)$^+$ and 879 (M)$^+$ corresponding to products 18 and 19, respectively. These spectroscopic data corroborate the structure 18 and 19 for these compounds.

It is evident that de-protection reaction of 15 using commercially available tetrabutylammonium fluoride (TBAF) in dry THF under nitrogen followed by reaction with triflic anhydride yielded triphenylene derivative 19 in 68% yield (entry 1, Table 2.1). Dry THF was used to curtail the amount of water in reaction mixture. Remarkably, when the deprotection reaction was carried out in the dry THF under oxygen atmosphere, followed by the reaction with triflic anhydride, derivative 19 was obtained in 73% yield (entry 2, Table 2.1). The structure of compound 19 was corroborated from its spectroscopic and analytical data.

### Table 2.1: Reaction conditions and yields of cyclized and uncyclized derivatives

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield % (19)*</th>
<th>Yield % (20)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>In dry THF; under N$_2$</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>In dry THF; under O$_2$</td>
<td>73</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>In THF: H$_2$O (95:5)</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>4.</td>
<td>THF: H$_2$O (90:10)</td>
<td>10</td>
<td>36</td>
</tr>
</tbody>
</table>

*These are the overall yields of deprotection followed by the sulfonylation with triflic anhydride.
Further, to see how the increase in water content in reaction mixture affect the ratio of cyclized to uncyclized derivatives, we carried out the deprotection reaction of derivative 15 in a mixture of THF:H$_2$O (95:5) (Scheme 2.7). The crude product obtained was used as such for the next reaction with triflic anhydride to furnish triphenylene derivative 19 and terphenyl derivative 20 in 25% and 30% yields (entry 3, Table 2.1), respectively. Further increase in percentage of water resulted in decrease in yield of cyclized triphenylene derivative 19. Formation of terphenyl derivative 20 shows obstruction to fluoride induced cyclization in aqueous THF. This may be attributed to lack of optimum electron density on phenolate oxygens required for cyclization due to spontaneous protonation of phenolate oxygens after fluoride induced desilylation.

To gain deeper insight into mechanism of the cyclization reaction, we also prepared a number of terphenyl derivatives 21a-21c (Schemes 2.8a and 2.8b) using the same synthetic methodology as that employed for terphenyls 14 and 15 and carried out their deprotection using TBAF. The derivative 21a was synthesized by the Pd(0) catalyzed Suzuki-Miyaura cross coupling of dibromo derivative 3 and boronic ester 10 in 82% yield (Scheme 2.8a). The $^1$H NMR spectrum of 21a showed two singlets (12H, 18H) at 0.25 and 1.02 ppm due to the tert-butyldimethylsilyl groups, two singlets (6H, each) at 3.58 and 3.84 ppm due to the methoxy groups, one doublet, one multiplet and one singlet (2H, 4H, 2H) at 6.53, 6.68-6.77 and 6.88 ppm due to terphenyl moiety. The FAB mass spectrum showed a parent ion peak at 611 (M)$^+$ corresponding to coupled product 21a.

Deprotection of 21a in the presence of TBAF and subsequent reaction with iodomethane provided 22a in 68% yield (Scheme 2.8a). The structure of derivative 22a was confirmed by $^1$H NMR which showed three singlets (6H, each) at 3.60, 3.85 and 3.94 ppm due to the methoxy groups, two singlets and one doublet (2H, 4H, 2H) at 6.58, 6.77 and 6.94 ppm for triphenylene moiety. The FAB mass spectrum of 22a showed a parent ion peak at 411 (M)$^+$. Similarly, we synthesized terphenyl derivatives 21b and 21c by Suzuki-Miyaura coupling of
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

dibromo derivative 4 with boronic esters 13a and 13b in 69% and 73% yield, respectively (Scheme 2.8b). The $^1$H NMR spectrum of 21b showed two singlets (12H, 18H) at 0.05 and 0.92 ppm due to the tert-butylidimethylsilyl groups, one singlet (6H) at 3.93 ppm due to methoxy groups, one multiplet, one double doublet, one singlet and one triplet (2H, 4H, 2H, 2H) at 6.60-6.62, 6.71, 6.89 and 7.08 ppm for the aromatic protons. The FAB mass spectrum of 21b showed a parent ion peak at 550 (M$^+$). The $^1$H NMR spectrum of compound 21c showed two singlets (12H, 18H) at 0.17 and 0.97 ppm due to the tert-butylidimethylsilyl groups, one singlet (6H) at 3.93 ppm due to methoxy groups, one doublet and two singlets (4H, 2H, 4H) at 6.67, 6.90 and 6.95 ppm for the aromatic protons. The FAB mass spectrum of 21c showed a parent ion peak at 550 (M$^+$). The structures of derivatives 21b and 21c were also confirmed by their conversion to triflate derivatives 22b (46%) and 22c (42%) (Scheme 2.8b).

![Scheme 2.8b: synthesis of terphenyl derivatifs 22b and 22c](image)

The $^1$H NMR spectrum of 22b showed one singlet (6H) at 3.96 ppm due to methoxy groups, one singlet and one multiplet (2H, 8H) at 6.89 and 6.94-7.35 ppm due to the aromatic protons. The $^1$H NMR spectrum of 22c showed one singlet (6H) at 3.96 ppm due to methoxy groups, one singlet and one multiplet (2H, 8H) at 6.90 and 7.11-7.17 ppm for the aromatic protons. The FAB mass spectra of both derivatives 22b and 22c showed parent ion peak at 586 (M$^+$). However, it was found that during the deprotection of 21a-21c to 22a-22c using TBAF, no aryl-aryl bond formation was observed as observed in case of compound 14 and 15. Although we were not surprised that 21a having two OTBS groups on the central aryl ring and 21b having OTBS groups meta to the ring closing site did not undergo cyclization, we were amazed that 21c having OTBS groups para to ring closing site did not lead to the formation of triphenylene during deprotection reaction. On the basis of these results, we may conclude that increased negative charge on phenolate oxygens after deprotection of -OTBS groups in terphenyls 14 and 15 provide an optimal amount of directing ability and electron density to complete cyclization. The cyclization is also enthalpically favoured by the greater
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

conjugation of planar triphenylene relative to terphenyl. A feasible mechanism for this cyclization involves a common phenolate anion intermediate obtained via fluoride-mediated desilylation. This intermediate then undergoes aerobic oxidation to form free radical which then rearranges to give quinone free radical followed by cyclization to triphenylene through oxidative dehydrogenation as shown in Scheme 2.9.

Since the cyclization of terphenyl 14 in the presence of fluoride ions was accompanied by drastic colour changes, we examined the behaviour of terphenyl 14 and 15 toward different anions by UV-vis and fluorescence spectroscopy. The UV-vis experiments were carried out in THF at $5.0 \times 10^{-5}$ M concentration of dosimeter 14 (Figure 2.2.). In the absence of anions, the absorption spectrum of receptor 14 is characterized by the presence of one absorption maximum peak at 295 nm.

Figure 2.2a. The UV-vis spectra of 14 ($5 \times 10^{-5}$ M) in the presence of TBAF (0 to 4.2 equiv.) in THF.

Figure 2.2b. The UV-vis spectra of 14 ($5 \times 10^{-5}$ M) in the presence of TBAF (4.2 to 50 equiv.) in THF.
Upon the addition of 0.0-4.2 equiv. of F\(^-\), the absorption band centered at 294 disappeared completely and new bands centered at 342 and 663 nm appeared (Figure 2.2a). On further addition of fluoride ions, the band at 663 nm decreased and three new bands centered at 879, 526 and 287 nm appeared with isosbestic points at 716, 582 and 315 nm, respectively (Figure 2.2b). The band at 287 nm is characteristic band for the triphenylene moiety. Thus, we propose that the spectral changes in Figure 2.2 are due to the formation of triphenylene moiety. These changes were clearly visible to the naked eye where the solution changes from colourless to violet (Figure 2.4A). However, there was absolutely no change in the absorption spectrum (Figure 2.3) or colour of receptor 14 (Figure 2.4B) in the presence of chloride, bromide, iodide, nitrate, acetate, cyanide, hydrogen phosphate and hydrogen sulfate ions, as their tetrabutylammonium salts, respectively at this particular concentration. We also used fluorescence spectroscopy to investigate the behaviour of terphenyl 14 in the presence of fluoride ions.

![Figure 2.3. UV-vis spectra of 14 (5 x 10^-5 M) in the presence of different anions (210 μM) in THF.](image)

![Figure 2.4. (A) The change in colour intensity of 14 (5 x 10^-5 M) upon the addition of F^- ions (from left to right, free ligand (14), 2, 4 and 6 equiv.) in THF. (B) Color changes of compound 14 (5 x 10^-5 M) in THF with the addition of different anions as their TBA salts: A=14, B=CN-, C=Cl-, D=Br-, E=I-, F=OAc-, G=HSO4-, H=NO3-, I=H2PO4-, J=F^-](image)

Hexasubstituted terphenyl 14 exhibited a fluorescence emission at 393 nm when excited at \(\lambda_{max}\) 294 nm. Upon addition of F\(^-\) ions, a red-shifted band appeared at 425 nm (a shift of 32 nm) with 32% enhancement of fluorescence emission (Figure 2.5A). The presence of fluoride ions results in cleavage of Si-O bond which increases negative charge on the
phenolate oxygen followed by cyclization to triphenylene as a result of which the conjugation is extended. This extended conjugation leads to the red shift and enhancement of fluorescence emission.

On further addition of F ions, fluorescene emission intensity was decreased (Figure 2.5B). This decrease in emission intensity may be ascribed to an electron transfer from phenolate oxygen to triphenylene moiety. It was found that 14 has a detection limit of 2 × 10⁻⁶ mol L⁻¹ for F⁻ which is sufficiently low for the detection of submillimolar concentration range of F⁻ ions found in many chemical systems. Similarly, we studied the behaviour of chemodosimter 15 towards the F⁻ ions by using UV-vis and fluorescence spectroscopy. The absorption spectrum of 15 exhibited a band at λₑₘ₃ 294 nm (Figure 2.6). Upon the addition of F⁻ ions (0 to 15 equiv.) to solution of 15 (5 × 10⁻⁵ M), broadening of band with blue shift at λₑₘ₃ 286 nm was observed.
In the fluorescence spectra, compound 15 exhibited an emission signal at 417 nm when excited at $\lambda_{\text{max}}$ 294 nm. Upon addition of 6 equiv. of F$^-$ ion, red shift of 30 nm (from 417 to 447 nm) was observed in emission band along with 44% increase in emission intensity (Figure 2.7) with a detection limit of $6 \times 10^{-7}$ mol L$^{-1}$. Under the same conditions as used for F$^-$ ions, we also tested the fluorescence response of compound 14 and 15 toward various anions (Cl$^-$, Br$^-$, I$^-$, OAc$^-$, HSO$_4^-$, NO$_3^-$, H$_2$PO$_4^-$, CN$^-$, OH$^-$, ClO$_4^-$, CO$_3^{2-}$, SO$_4^{2-}$) but no significant spectral changes occurred in the presence of these anions (Figure 2.8 for 14 and Figure 2.9 for 15, red bars).

To test the practical applicability of both chemodosimeters as F$^-$ selective sensors, competitive experiments were carried out in the presence of F$^-$ ions mixed with various anions, no significant variation in fluorescence behaviour was observed by comparison with or without the other anions besides F$^-$ ions (Figure 2.8 and 2.9, grey bars). Thus, these UV-vis and fluorescence changes indicate that protected terphenyl 14 and 15 can also be exploited for the development of fluoride sensor. We also synthesized symmetrically substituted triphenylene derivative 14a as model compound. The compound 14a was synthesized by the alkylation of hexahydroxytriphenylene with tert-butyldimethylsilyl chloride in the presence of imidazole in 89% yield (Scheme 2.10). The structure of compound 14a was confirmed by the NMR spectroscopy. The $^1$H NMR spectrum of compound 14a shows two singlets (36H, 54H) at 0.30 and 1.05 ppm for the protons of tert-butyldimethylsilyl groups and one singlet (6H) at 7.76 ppm for the aromatic protons. The FAB mass spectrum showed a parent ion peak at 1009 (M$^+$) corresponding to product 14a.
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

These spectroscopy data corroborate the structure 14a for the model compound. We evaluated the behaviour of 14a toward the F⁻ ions by using the UV-vis and fluorescence spectroscopy. The UV-vis spectrum of compound 14a exhibited two strong absorption bands at $\lambda_{\text{max}}$ 275 nm and 266 nm (Figure 2.10a). Upon the addition of increasing amounts of F⁻ ions (as its tetrabutylammonium salt), a decrease in absorption intensity of both the bands was observed and two new bands appeared at $\lambda_{\text{max}}$ 348 nm and 661 nm (Figure 2.10a).

Figure 2.10a. The UV-vis spectra of 14a ($5 \times 10^{-5}$ M) in the presence of TBAF (0 to 6.5 equiv.) in THF.

Figure 2.10b. The UV-vis spectra of 14a ($5 \times 10^{-5}$ M) in the presence of TBAF (6.5 to 20 equiv.) in THF.
which goes on increasing in intensity up to the addition of 6.5 equiv. of F$^-$ ions. However, further addition of fluoride ions leads to decrease in the intensity of bands at 348 nm and 661 nm with simultaneous appearance of new bands at 517 and 872 nm (Figure 2.10b). The absorption of bands at 517 and 872 nm goes on increasing up to the addition of 20 equiv. of F$^-$ ions. So, three isobestic points were observed at 704, 584 and 384 nm. These changes in the absorption spectra are exactly similar to results previously shown in Figure 2.2. This further corroborates our finding that terphenyl derivative 14 undergoes cyclization in the presence of TBAF to give triphenylene derivative 17a.

2.2.2. Synthesis of unsymmetrically substituted triphenylene derivatives having crown moieties

Recently, design and synthesis of discotic mesogens carrying crown ether moiety has attracted great research interests. Attachment of crown ether as substituent to mesogenic building blocks gives access to novel hybrid materials as complexation of crown ethers with metal salts leads to a significant stabilization of the mesophase. However, literature reports shows that the synthesis of unsymmetrically substituted triphenylene derivatives having crown moiety on large scale using conventional oxidizing agents is inconvenient as ether hydrolysis is a known side reaction$^{21}$ in such oxidative couplings employing FeCl$_3$ and this pathway accounts for the majority of side products. An alternative route employing photochemical cyclization for synthesis of derivatives having crown moiety is so slow$^{22}$ that conversion of less than 5% was achieved after 4 weeks irradiation. Another route involving preparation of the crown ether in the final step involves many steps and lower yields. In section 2.2.1, we discussed about the synthesis of symmetrically and unsymmetrically substituted triphenylene derivatives by fluoride induced cyclization. In continuation of this investigation, we have now synthesized unsymmetrically substituted triphenylene derivatives having crown moiety using the fluoride-induced cyclization in good yield without the formation of any side products.

The base catalyzed tosylation of tetraethylene glycol 23 with p-toluenesulphonyl chloride (p-TsCl) in the presence of THF:H$_2$O mixture gave tetraethyleneglycol ditosylate 24 in 69% yield. Reaction of compound 24 with 4,5-dibromobenzene-1,2-diol 2 in dry DMF in the presence of potassium carbonate and 18-crown-6 as a catalyst furnished derivative 25 in 57% yield (Scheme 2.11). The $^1$H NMR spectrum of 25 showed one singlet (6H) at 1.26 due to the methyl group of p-toluenesulphonyl moiety, one multiplet and one triplet (12H, 4H) at
3.59-3.62 and 4.16 ppm corresponding to the protons of crown moiety and two doublets (2H, each) at 7.33 and 7.179 ppm due to the aromatic protons.

Further, palladium catalyzed Suzuki-Miyaura cross coupling between compound 25 and boronic ester 9 furnished terphenyl derivative 26 in 63% yield as shown in Scheme 2.12. The structure of compound 26 was confirmed from its spectroscopic and analytical data. The \(^1\)H NMR spectrum of 26 showed four singlets (12H, 12H, 18H, 18H) at 0.06, 0.17, 0.93 and 0.97 ppm due to tert-butyldimethylsilyl moiety, one singlet and two triplets (8H, 4H, 4H) at 3.77, 3.92 and 4.18 ppm due to the protons of crown moiety, one doublet, one multiplet and one singlet (2H, 4H, 2H) at 6.52, 6.61-6.64 and 6.82 ppm due to the aromatic protons.

The ESI mass spectrum showed a parent ion peak at MS \(\text{ESI m/z 941 (M)}^+\). These spectroscopic data corroborates the structure 26 for this compound. In the next step for the synthesis of compound 27, we adopted a two step one pot strategy wherein deprotection using tetrabutylammonium fluoride (TBAF) in dry THF and subsequent reaction with lauryl chloride furnished compound 27 in 62% yield. The \(^1\)H NMR spectrum of 27 showed two singlets (64H, 8H) at 1.29 and 1.81 ppm and two triplets (12H, 8H) at 0.89 and 2.64 ppm.
corresponding to the protons of lauryl group, three singlets (8H, 4H, 4H) at 3.81, 4.03 and 4.35 ppm due to the protons of crown moiety, one singlet, one doublet (2H, 4H) at 7.69 and 8.18 ppm due to the aromatic protons. The MALDI-TOF mass spectrum showed a parent ion peak at 1233.7 (M+Na)+. These spectroscopic data corroborate the structure 27 for this compound. Similarly, we synthesized the bis-terphenyl derivative 29. The synthesis involves the bromination of dibenzo-18-crown-6 with Br₂ in dry CH₂Cl₂ to give tetrabromo derivative 28 in 91% yield. The ¹H NMR spectrum of 28 showed two triplets (8H, each) at 4.18 and 4.36 ppm due to crown moiety and one singlet (4H) at 6.99 ppm for the aromatic protons. Palladium(0) catalyzed Suzuki-Miyaura cross coupling of bromo derivative 28 with boronic ester 9 gave coupled product 29 in 68% yield (Scheme 2.13).

The ¹H NMR spectrum of bis-terphenyl derivative 29 showed four singlets (24H, 24H, 36H, 36H) at 0.07, 0.17, 0.93 and 0.97 ppm due to protons of tert-butyldimethylsilyl groups, two singlets (8H, 8H) at 4.04 and 4.22 ppm due to crown moiety, one doublet and two singlets (8H, 4H, 4H) at 6.52, 6.61 and 6.83 ppm corresponding to the aromatic protons. The FAB mass spectrum showed a parent ion peak at 1705.9 (M)+. These spectroscopic data corroborate the structure 29 for this compound. Deprotection of bis-terphenyl 29 using TBAF and its subsequent reaction with lauryl chloride yielded triphenylene derivative 30 in 63% yields (Scheme 2.13). The structure of derivative 30 was characterized from its spectroscopic data. The ¹H NMR spectrum of 30 showed four singlets (24H, 128H, 16H, 16H) at 0.89, 1.29,
1.79 and 2.62 ppm due to the protons of lauryl group, two singlet (8H, 8H) at 4.12 and 4.38 ppm due to crown moiety, two singlet (4H, 8H) at 7.66 and 8.11 ppm due to aromatic protons. The FAB mass spectrum showed a parent ion peak at 2268.37 (M+Na)^+. These spectroscopic data corroborate the structure 30 for this compound. We studied the sensing behaviour of derivatives 26 and 29 toward different anions using UV-vis and fluorescence spectroscopy. The UV-vis experiments of compounds 26 (5 × 10^{-5} M) and 29 (5 × 10^{-5} M) were carried out in THF by adding aliquots of F^- ions. In the absence of F^- ions, the UV-vis spectra of both compounds showed absorption bands at \(\lambda_{\text{max}}\) 294 nm. Upon the addition of F^- ions to the solution of compound 26 in THF, broadening of absorption band was observed (Figure 2.11) with gradual change of colour from colourless to yellowish brown visible to naked eye (Figure 2.11, inset).

![Figure 2.11](image)

**Figure 2.11.** The UV-vis spectrum of 26 (5 × 10^{-5} M) in the presence of TBAF (0 to 25 equiv.) in THF.

![Figure 2.12](image)

**Figure 2.12.** The UV-vis spectral changes of 29 (5 × 10^{-5} M) in the presence of TBAF (0-6 equiv.) in THF (inset show the SEM image of nanoaggregates).
On the other hand, addition of incremental amounts of F− ions to the solution of compound 29 leads to broadening of band at \( \lambda_{\text{max}} \) 294 nm with light-scattering tails in the long wavelength region (Figure 2.12). These light-scattering tails are attributed to Mie scattering, suggesting the presence of nanosized particles. The formation of these aggregates upon the addition of F− ions was further investigated by scanning electron microscopy (SEM) image which shows the presence of nanoaggregates (Figure 2.12, inset). In the fluorescence spectrum, compound 26 exhibited an emission band at 417 nm when excited at \( \lambda_{\text{max}} \) 294 nm. Upon addition of 6 equiv. of F− ions to the solution of 26 (5 × 10⁻⁶ M), emission band was red shifted to 445 nm (\( \Delta \lambda_{\text{max}} \) 28 nm) (Figure 2.13).

In case of compound 29, under similar set of conditions, addition of 8 equiv. of F− ions to the solution of 29 (5 × 10⁻⁶ M), the emission band was red shifted to 447 nm (\( \Delta \lambda_{\text{max}} \) 30 nm) along...
with enhancement of emission intensity (Figure 2.14). The detection limits of compounds 26 and 29 for F\(^{-}\) ions were found to be 7.5 \times 10^{-7} \text{ mol L}^{-1} and 5 \times 10^{-7} \text{ mol L}^{-1}, respectively. Under the same conditions as used for F\(^{-}\) ions, we also tested the fluorescence response of compounds 26 and 29 toward various anions like Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), CN\(^{-}\), OAc\(^{-}\), HSO\(_4\)\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^{-}\), H\(_2\)PO\(_4\)\(^{-}\), OH\(^{-}\), ClO\(_4\)\(^{-}\) and CO\(_3\)\(^{2-}\), but no significant spectral changes occurred in the presence of these anions (Figure 2.15 and Figure 2.16). To test the practical applicability of these compounds as F\(^{-}\) selective sensors, competitive experiments were carried out in the presence of F\(^{-}\) at 30 µM mixed with Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), CN\(^{-}\), OAc\(^{-}\), HSO\(_4\)\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\), H\(_2\)PO\(_4\)\(^{-}\), OH\(^{-}\), ClO\(_4\)\(^{-}\) and CO\(_3\)\(^{2-}\) at 60 µM, no significant variation in fluorescence behaviour was observed by comparison with or without the other anions besides F\(^{-}\) (Figure 2.17 and Figure 2.18). Thus from these studies we may conclude that both derivatives 26 and 29 act as highly selective and sensitive chemodosimeters for the F\(^{-}\) ions over the other anions tested.
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

Figure 2.18. Competitive selectivity of 29 (5 \times 10^{-6} M) towards F^- in the presence of different anions in THF. (A=F, B=Cl, C=Br, D=I, E=CN, F=HSO_4, G=H_2PO_4, H=NO_3, I=OAc, J=OH, K=ClO_4, L=CO_3^{2-}, M=SO_4^{2-})

Further compound 30 showed self-assembly behaviour as it forms stable fluorescent organogel in non-polar solvent like cyclohexane (Table 2.2). The organogel shows the sol-gel transition with respect to temperature (Figure 2.19). Thermal stability of the gel was studied by the dropping-ball method. T_{gel}, the required temperature for the organogel to collapse, increases with an increase in concentration of gelator 30 (Figure 2.20). The self-assembly behaviour was studied by the polarized optical microscope (POM) and scanning electron micrograph (SEM). The polarized optical micrographs of organogel showed birefringence at room temperature (Figure 2.21a).

Figure 2.19. Sol-gel transition with respect to temperature

Figure 2.20. Variation of T_{gel} with increase in the concentration of the gelator 30 in cyclohexane.

Table 2.2: Gelation behaviour of derivative 30 in different solvents

<table>
<thead>
<tr>
<th>Solvent used</th>
<th>Gelation behaviour of 30</th>
<th>Amount (mg)</th>
<th>T_{gel} (°C) in cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>G</td>
<td>5.0</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>10.0</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>15.0</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>20.0</td>
<td>57</td>
</tr>
</tbody>
</table>
Derivative 30 displayed clearing point at 200 °C (Figure 2.21b). Upon cooling from isotropic phase it showed an irregular texture with small grains down to the room temperature (Figure 2.21c-d). The morphology of organogel of gelator 30 was studied by the SEM analysis which showed the rod-like structures as shown in Figure 2.21e-f.

2.2.3. Synthesis of symmetrically substituted extended triphenylene derivative

Literature reports show that presence of larger aromatic cores influences the mesomorphic properties of discotic liquid crystals. These aromatic cores form columnar mesophase which have high mobilities along the axis of column. However, the synthesis of extended triphenylene like triphenylene by the oxidative cyclization using oxidizing agents is very difficult due to the insolublity of these oxidizing agents in common organic solvents. Thus, the isolation of products from the reaction mixture becomes very difficult. In continuation of our work on the synthesis of triphenylene derivatives, we have also synthesized extended triphenylene derivative in good yield using fluoride-induced cyclization as was used in the synthesis of triphenylene derivatives. The bromination of triphenylene 31 with Br₂ in the
presence of iron powder and nitrobenzene gave 2,3,6,7,10,11-hexabromotriphenylene 32 in 92% yield (Scheme 2.14).

![Scheme 2.14: Synthesis of hexabromotriphenylene derivative 32](image)

Palladium catalyzed Suzuki-Miyaura cross coupling of hexabromotriphenylene 32 with boronic ester 9 furnished extended triphenylene derivative 33 in 81% yield (Scheme 2.15). The structure of compound 33 was confirmed from its spectroscopic and analytical data. The $^1$H NMR spectrum of 33 showed four singlets (36H, 36H, 54H, 54H) at δ 0.10, 0.21, 0.95 and 1.00 ppm due to tert-butyldimethylsilyl (TBS) moiety, one multiplet, one doublet and one singlet (12H, 6H, 6H) at 6.71-6.76, 6.84 and 8.56 ppm, corresponding to the aromatic protons. The FAB mass spectrum showed a parent ion peak at 2248 (M)$^+$ corresponding to coupled product 33. These spectroscopic data corroborates the structure 33 for this compound.

![Scheme 2.15: Synthesis of extended triphenylene derivative 33](image)

Further, the treatment of extended triphenylene derivative 33 with tetrabutylammonium fluoride and its subsequent reaction with triflic anhydride furnished supertriphenylene 34 in 72% yield, where three C-C bonds are formed in single step (Scheme 2.16). The $^1$H NMR spectrum of 34 showed three singlets (6H, 6H, 6H) at 8.58, 9.12 and 9.92 ppm due to the aromatic protons. The FAB mass spectrum showed a parent ion peak at 2456 (M)$^+$. These spectroscopic data corroborates the structure 34 for this compound. In the next step, we
carried out the deprotection of -OTBS groups. The negative charge on phenolate oxygens after deprotection of -OTBS groups in derivative 33 provide optimum electron density for cyclization.

The deprotection reaction of compound 33 with TBAF was accompanied by significant color change; this prompted us to examine the behaviour of derivative 33 in the presence of F⁻ ions using UV-vis and fluorescence spectroscopy. The UV-vis experiments were carried out in THF at 1 × 10⁻⁵ M concentration of compound 33 (Figure 2.22). In the absence of F⁻ ions, the compound 33 showed absorption band at 306 nm which undergoes red shift to 325 nm (Δλ 19 nm) upon the addition of 15 equiv. of F⁻ ions.

These absorption changes are accompanied by change in color of the solution from colorless to green (Figure 2.22, inset). However, there was no change in the absorption spectra of 33
upon the addition of other anions such as Cl\(^-\), Br\(^-\), I\(^-\), CN\(^-\), AcO\(^-\), NO\(_3^-\), H\(_2\)PO\(_4^+\), HSO\(_4^-\), OH\(^-\) and ClO\(_4^-\) (Figure 2.23). We also used the fluorescence spectroscopy to investigate the behaviour of 25 in the presence of F\(^-\) ions. The THF solution (1.0 × 10\(^{-6}\) M) of derivative 33 exhibited strong emission at \(\lambda_{\text{max}}\) 395 nm and complete quenching of the emission band was observed upon addition of 12 \(\mu\)M of F\(^-\) ions (Figure 2.24).

The complete fluorescence quenching may be ascribed to an electron transfer from phenolate oxygen to triphenylene moiety. It was found that compound 33 has a detection limit of 8 × 10\(^{-7}\) mol L\(^{-1}\) for F\(^-\) which is sufficiently low for the detection of submillimolar concentration range of F\(^-\) ions. Under the same conditions as used for F\(^-\) ions, we also tested the fluorescence response of compound 33 toward various other anions such as Cl\(^-\), Br\(^-\), I\(^-\), CN\(^-\), AcO\(^-\), NO\(_3^+\), H\(_2\)PO\(_4^+\), HSO\(_4^-\), OH\(^-\) and ClO\(_4^-\) but no significant change in the fluorescence spectra (Figure 2.25) or colour of solution of 33 (Figure 2.26) was observed in the presence of these anions.

![Figure 2.24](image_url)  
**Figure 2.24** The fluorescence quenching of 33 (1 × 10\(^{-6}\) M) upon the addition of incremental amount of TBAF (0–15 equiv.) in THF. The inset shows fluorescence quenching upon the addition F\(^-\) ions.

![Figure 2.25](image_url)  
**Figure 2.25** Selectivity of 33 (1 × 10\(^{-6}\) M) toward F\(^-\) ions in the presence of other anions in THF. (A, F\(^-\); B, Cl\(^-\); C, Br\(^-\); D, I\(^-\); E, CN\(^-\); F, HSO\(_4^-\); G, H\(_2\)PO\(_4^-\); H, NO\(_3^-\); I, OAc\(^-\); J, OH\(^-\); K, ClO\(_4^-\))

![Figure 2.26](image_url)  
**Figure 2.26.** (A) Fluorescence turn-off and (B) Color changes of compound 33 (5 × 10\(^{-6}\) M) in THF with the addition of different anions as their TBA salts: (A, F\(^-\); B, Cl\(^-\); C, Br\(^-\); D, I\(^-\); E, CN\(^-\); F, HSO\(_4^-\); G, H\(_2\)PO\(_4^-\); H, NO\(_3^-\); I, OAc\(^-\); J, OH\(^-\); K, ClO\(_4^-\))
To test the practical applicability of compound 33 as F⁻ selective sensor, competitive experiments were carried out in the presence of F⁻ at 12 µM mixed with Cl⁻, Br⁻, I⁻, CN⁻, AcO⁻, NO₃⁻, H₂PO₄⁻, HSO₄⁻, OH⁻ and ClO₄⁻ at 200 µM, no significant variation in fluorescence behaviour was observed by comparison with or without the other anions besides F⁻ (Figure 2.27).

This result shows that extended triphenylene derivative 33 acts as selective chemodosimeter for the F⁻ ions over the other anions such as Cl⁻, Br⁻, I⁻, CN⁻, AcO⁻, NO₃⁻, H₂PO₄⁻, HSO₄⁻, OH⁻ and ClO₄⁻. Further, to check the practical applicability of compound 33 for detection of fluoride in water, we prepared a TLC strip by immersing it in the solution of 33 in THF. After drying it in air, the strip was then immersed in aqueous solution of potassium fluoride, an instant colorimetric change was observed which indicates sensing of fluoride ions (Figure 2.28a).

Thus, this fluorescent switching can be used for instant detection of fluoride ions in aqueous media. Since the presence of fluoride ions leads to development of negative charge on the phenolate oxygen atoms of the triphenylene, we further investigated the sensing properties of
compound 33 in presence of F⁻ ions toward different metal ions such as Na⁺, K⁺, Zn²⁺, Cd²⁺, Ag⁺, Pb²⁺, Cu²⁺, Co²⁺, Ni²⁺, Hg²⁺, Ca²⁺ and Mg²⁺ by fluorescence spectroscopy. Interestingly, the addition of 15 µM of Hg²⁺ ions as its perchlorate salt to solution of 33 (1.0 × 10⁻⁶ M) containing 15 µM of F⁻ ions results in revival of fluorescence emission at 412 nm (Figure 2.29).

![Figure 2.29. The Fluorescence spectra of compound 33 (1 × 10⁻⁶ M) upon the addition of Hg²⁺ ions (15 equiv.) after addition of 15 equiv. of TBAF in THF.](image)

However, no such significant revival was observed on addition of 15 µM of other metal ions such as Na⁺, K⁺, Zn²⁺, Cd²⁺, Ag⁺, Pb²⁺, Cu²⁺, Co²⁺, Ni²⁺, Hg²⁺, Ca²⁺ and Mg²⁺, as their perchlorate salts to the THF solution of compound 25 in presence of F⁻ ions under similar conditions (Figure 2.30). This indicates that intermediate formed after the desilylation has strong interaction for mercury ions over the other anions.

2.3. Conclusion

In conclusion, we synthesized terphenyl based derivatives 14, 15, 26 and 29 having –OTBS groups by palladium(0) catalyzed Suzuki-Miyaura cross coupling. These derivatives upon deprotection of OTBS groups using TBAF undergo cyclization to give symmetrically/unsymmetrically substituted analogues triphenylenes derivatives 18, 19, 27 and 30. Using the same strategy, we have also synthesized the supertriphenylene 34 from extended triphenylene derivative 33. Further, all these derivatives act as highly sensitive and selective chemodosimeters for fluoride ions over the other anions such as Cl⁻, Br⁻, I⁻, CN⁻, OAc⁻, HSO₄⁻, SO₄²⁻, NO₃⁻, H₂PO₄⁻, OH⁻, ClO₄⁻ and CO₃²⁻.
2.4. Experimental

2.4.1. General methods and instrumentation

**Physical measurements:** Most of the chemicals and reagents were obtained from Sigma-Aldrich and were used as such without further purification. Solvents for carrying out reactions and analytical studies were dried prior to use. Tetrahydrofuran (THF) was dried by refluxing it over sodium metal and benzophenone for 5 h and then fractionally distilled. Dichloromethane was shaken with portions of conc. H$_2$SO$_4$ until the acid layer remained colorless, washed with water, aqueous 5% Na$_2$CO$_3$ and then with water again. Pre-dried with CaCl$_2$ and then distilled from CaSO$_4$ to get dry dichloromethane. Melting points were determined in capillaries and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on JOEL-FT NMR-AL 300 MHz spectrophotometer using CDCl$_3$/CD$_3$COCD$_3$/C$_4$D$_8$O/DMSO-$d_6$ as solvent and TMS as internal standards. Data are recorded as fellow: chemical shifts in ppm ($\delta$), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet), coupling constants (Hz), integration, and interpretation. Elemental analysis was done using Flash EA 1112 CHNS-O analyzer of Thermo Electron Corporation. UV-vis spectra were recorded on SHIMADZU UV-2450 PC spectrophotometer with a quartz cuvette (path length 1 cm). The cell holder was thermostatted at 25 °C. All the fluorescence spectra were recorded on SHIMADZU RF-5301 PC spectrofluorometer. MALDI-TOF spectra were recorded on a Bruker Daltonics flexAnalysis instrument. FAB mass spectra were recorded on a JEOL SX 102/Da-600 mass spectrometer.

2.4.2. UV-vis and Fluorescence titrations

UV-vis and fluorescence titrations were performed using 5.0 $\times$ 10$^{-5}$ M and 5.0 $\times$ 10$^{-6}$ M concentration of ligands in THF, respectively. Standard solutions (10$^{-1}$ M to 10$^{-3}$ M) of tetrabutylammonium salts of various anions like F, Cl, Br, I, CN, HSO$_4$, H$_2$PO$_4$, NO$_3$, OAc$^-$ were prepared in dry THF. Typically, the aliquots of these freshly prepared standard solutions were added to 3 mL solution of ligands and the UV-vis and fluorescence spectra were recorded.

2.4.3. Synthesis of various terphenyl and triphenylene derivatives

**Synthesis of 4,5-dibromobenzene-1,2-diol (2)**

To a solution of catechol 1 (5 g, 45.45 mmol) in CCl$_4$ (50 mL) was added bromine (15.27 g, 95.44 mmol) and the reaction mixture was allowed to stir overnight. After completion of the reaction (TLC), light brown coloured solid
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

separated out. The solid was filtered off, washed with excess CCl₄ and dried in vacuum to get the compound 2 in 86% yield. Mp: 118-120 °C (Lit. value 119-121°). ¹H NMR (300 MHz, CDCl₃, ppm): δ 5.32 (s, 2H, OH), 7.21 (s, 2H, ArH).

Synthesis of (4,5-dibromo-1,2-phenylene)bis(oxy)bis(tert-butyldimethylsilane) (3)

To a solution of 4,5-dibromobenzene-1,2-diol 2 (2.0 g, 7.46 mmol) in DMF (20 mL) was added imidazole (1.52 g, 22.38 mmol). The reaction mixture was stirred at room temperature for 10-15 minutes and then tert-butyldimethysilylchloride (3.38 g, 22.38 mmol) was added to the above solution in portions. The reaction mixture was stirred for 12 h at room temperature. On completion of the reaction (TLC), the mixture was extracted with ethyl acetate twice. The organic layer was separated out, washed with brine, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure to give a residue which was purified by column chromatography over silica gel (hexane) to give compound 3 as pale yellow liquid in 94% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.02 (s, 12H, -Si(CH₃)₂), 0.80 (s, 18H, -C(CH₃)₃), 6.88 (s, 2H, ArH).

Synthesis of 1,2-dibromo-4,5-dimethoxybenzene (4)

To a solution of 4,5-dibromobenzene-1,2-diol 2 (2.0 g, 7.46 mmol) and K₂CO₃ (3.08 g, 22.38 mmol) in dry CH₂Cl₂ (30 mL) was added methyl iodide (5.29 g, 37.31 mmol). The reaction mixture was heated at 45°C for 24 h. After completion of reaction (TLC), the solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO₂, ethyl acetate/hexane 5:95) to give 4 as waxy solid in 90% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.85 (s, 6H, -OCH₃), 7.05 (s, 2H, ArH).

Synthesis of 4-bromobenzene-1,2-diol (6)

4-bromo-1,2-dimethoxybenzene 5 (2.0 g, 9.21 mmol) was dissolved in dry DCM (28 mL) and the reaction mixture was cooled down to -78 °C using liquid nitrogen. BBr₃ (7.22 g, 28.8 mmol) was added drop wise to the stirred solution, maintaining the temperature at -78 °C. After the complete addition, the mixture was then allowed to stirred stirred overnight at room temperature. After completion of reaction (TLC), reaction mixture was quenched with water and extracted with DCM. The organic layer was separated out, washed with brine, dried over MgSO₄ and filtered. The filtrate was
evaporated to dryness under reduced pressure to give compound 6 in 86% yield. The compound 6 was used as such for the next step.

**Synthesis of (4-bromo-1,2-phenylene)bis(oxy)bis(tert-butyldimethylsilane) (7)**

To a solution of 4-bromobenzene-1,2-diol 6 (1.5 g, 7.93 mmol) in DMF (10 mL) was added imidazole (1.61 g, 23.79 mmol). The reaction mixture was stirred for 10-15 minutes at room temperature. TBDMSCl (3.59 g, 23.79 mmol) was then added to reaction mixture in portions and the mixture was stirred at room temperature for 12 hours. After completion of the reaction (TLC), reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over MgSO₄, and filtered. The filtrate was evaporated to dryness under reduced pressure to give residue which was purified by column chromatography over silica gel (hexane) to give compound 7 as liquid in 60% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.17 (s, 6H, -Si(CH₃)₂), 0.20 (s, 6H, -Si(CH₃)₂), 0.97 (s, 9H, -C(CH₃)₃), 0.98 (s, 9H, -C(CH₃)₃), 6.89-7.00 (m, 2H, ArH), 6.68 (d, J = 8.4 Hz, 1H, ArH).

**Synthesis of (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-phenylene)bis(oxy)bis(tert-butyldimethylsilane) (9)**

To a suspension of [PdCl₂(PPh₃)₂] (184 mg, 0.26 mmol) and 7 (2.5 g, 5.98 mmol) in 1,4-dioxane (10 mL) was added 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8 (2.29 g, 17.94 mmol), and triethylamine (1.81 g, 17.94 mmol) under nitrogen. The resulting reaction mixture was stirred at 80 °C for 5 hours. After the completion of reaction (TLC), the dioxane was removed under reduced pressure. To the resulting residue water and dichloromethane were added. The organic layer was separated out, washed with brine, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness under vacuum to get the crude which was purified by column chromatography using hexane as an eluent to give compound 9 as pale yellow oily liquid in 57% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.19 (s, 12H, -Si(CH₃)₂), 0.98 (s, 18H, -C(CH₃)₃), 1.31 (s, 12H, -CH₃), 7.03-7.10 (m, 3H, ArH). ¹³C NMR (75.45 MHz, CDCl₃, ppm): δ -4.14, -4.08, 18.26, 24.71, 25.90, 83.87, 120.38, 145.91, 147.48. MS (ESI) m/z: 464.28. Elemental analysis: calcd. for C₂₄H₄₅BO₄Si₂: C 62.04, H 9.76; Found: C 62.23, H 9.83.
Synthesis of 2-(3,4-dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)

To a suspension of [PdCl$_2$(PPh$_3$)$_2$] (387.5 mg, 0.55 mmol) and 4-bromo-1,2-dimethoxybenzene 5 (3.0 g, 13.82 mmol) in 1,4-dioxane (10 mL) was added 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8 (5.3 g, 41.47 mmol), and triethylamine (4.18 g, 41.46 mmol) under nitrogen. The resulting reaction mixture was stirred at 80°C for 5 hours. After the completion of reaction (TLC), the dioxane was removed under reduced pressure. To the resulting residue water and dichloromethane were added. The organic layer was separated out, washed with brine, dried over MgSO$_4$ and filtered. The filtrate was evaporated to dryness under vacuum to get the crude which was purified by column chromatography (SiO$_2$, ethyl acetate/hexane 5:95) to give waxy solid compound 10 in 55% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 1.34 (s, 12H, -CH$_3$), 3.90 (s, 3H, -OCH$_3$), 3.92 (s, 3H, -OCH$_3$), 6.88 (d, J = 8.1 Hz, 1H, ArH), 7.28 (s, 1H, ArH), 7.42 (d, J = 8.1 Hz, 1H, ArH). $^{13}$C NMR δ (75.45 MHz, CDCl$_3$, ppm): δ 24.78, 55.67, 55.77, 83.59, 110.38, 116.43, 128.48, 148.24, 151.53. MS (ESI) m/z: 265.28. Elemental analysis: calcd. for C$_{14}$H$_{21}$BO$_4$: C 63.66, H 8.01; Found: C 63.58, H 7.99.

Synthesis of (3-bromophenoxy)(tert-butyl)dimethylsilane (12a)

To a solution of 3-bromophenol 11a (3.0 g, 17.34 mmol) in DMF (25 mL) was added imidazole (2.36 g, 34.68 mmol). The reaction mixture was stirred for 10-15 minutes at room temperature. Then TBDMSOCl (3.93 g, 26.01 mmol) was added to reaction mixture in portion wise and the mixture was stirred at room temperature for 12 hours. After completion of the reaction (TLC), reaction mixture was extracted with ethyl acetate and water. The organic layer was separated out, washed with brine, dried over MgSO$_4$, and filtered. The filtrate was evaporated to dryness under reduced pressure and column chromatography over silica gel (hexane) was carried out to give compound 12a as pale yellow liquid in 89% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.18 (s, 6H, -Si(CH$_3$)$_2$), 0.96 (s, 9H, -C(CH$_3$)$_3$), 6.75 (t, J = 3.4 Hz, 1H, ArH), 6.97-6.99 (m, 1H, ArH), 7.05-7.07 (m, 2H, ArH).

Synthesis of (4-bromophenoxy)(tert-butyl)dimethylsilane (12b)

To a solution of 4-bromophenol 11b (3.0 g, 17.34 mmol) in DMF (25 mL) was added imidazole (2.36 g, 34.68 mmol). The reaction mixture was stirred for 10-15 minutes at room temperature. Then TBDMSOCl (3.93 g, 26.01 mmol) was added to reaction mixture in portion wise and the mixture was stirred at room temperature for 12 hours. After completion of the reaction (TLC), reaction mixture was extracted with ethyl acetate and water. The organic layer was separated out, washed with brine, dried over MgSO$_4$, and filtered. The filtrate was evaporated to dryness under reduced pressure and column chromatography over silica gel (hexane) was carried out to give compound 12b as pale yellow liquid in 89% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.18 (s, 6H, -Si(CH$_3$)$_2$), 0.96 (s, 9H, -C(CH$_3$)$_3$), 6.75 (t, J = 3.4 Hz, 1H, ArH), 6.97-6.99 (m, 1H, ArH), 7.05-7.07 (m, 2H, ArH).
g, 26.01 mmol) was added to reaction mixture in portions wise and the mixture was stirred at room temperature for 12 hours. After completion of the reaction (TLC), reaction mixture was extracted with ethyl acetate and water. The organic layer was separated out, washed with brine, dried over MgSO₄, and filtered. The filtrate was evaporated to dryness under reduced pressure and column chromatography over silica gel (hexane) was carried out to give compound 12b as pale yellow liquid in 92% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.16 (s, 6H, -Si(CH₃)₂), 0.95 (s, 9H, -C(CH₃)₃), 6.69 (d, J = 6.59 Hz, 2H, ArH), 7.29 (d, J = 6.75 Hz, 2H, ArH).

**Synthesis of tert-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)silane (13a)**

To a suspension of [PdCl₂(PPh₃)₂] (315 mg, 0.45 mmol) and (3-bromophenoxy)(tert-butyldimethylsilane 12a (3.3 g, 11.49 mmol) in 1,4-dioxane (10 mL) was added 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-8 (4.41 g, 34.47 mmol), and triethylamine (3.48 g, 34.47 mmol) under nitrogen. The resulting reaction mixture was stirred at 80°C for 5 hours. After the completion of reaction (TLC), the dioxane was removed under reduced pressure. The resulting residue was extracted with water and dichloromethane. The organic layer was separated out, washed with brine, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness under vacuum to get the crude which was purified by column chromatography (SiO₂, DCM/hexane 20:80) to give compound 13a as pale yellow oil in 62% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.02 (s, 6H, -Si(CH₃)₂), 0.99 (s, 9H, -C(CH₃)₃), 1.26 (s, 12H, -CH₃), 6.85 (s, 1H, ArH), 6.95 (d, J = 8.0 Hz, 1H, ArH), 7.29-7.32 (m, 2H, ArH).

**Synthesis of tert-butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)silane (13b)**

To a suspension of [PdCl₂(PPh₃)₂] (315 mg, 0.45 mmol) and (4-bromophenoxy)(tert-butyldimethylsilane 12b (3.3 g, 11.49 mmol) in 1,4-dioxane (10 mL) was added 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-8 (4.41 g, 34.47 mmol), and triethylamine (3.48 g, 34.47 mmol) under nitrogen. The resulting reaction mixture was stirred at 80°C for 5 hours. After the completion of reaction (TLC), the dioxane was removed under reduced pressure. To the resulting residue water and dichloromethane were added. The organic layer was separated out, washed with brine, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness
under vacuum to get the crude which was purified by column chromatography (SiO₂, DCM/hexane 25:75) to give compound 13b as pale yellow oil in 67% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.02 (s, 6H, -Si(CH₃)₂), 0.78 (s, 9H, -C(CH₃)₃), 1.13 (s, 12H, -CH₃), 6.64 (d, J = 8.4 Hz, 2H, ArH), 7.50 (d, J = 8.4 Hz, 2H, ArH).

Synthesis of terphenyl derivative (14)

To a mixture of 3 (687 mg, 1.38 mmol) and tetrakis(triphenylphosphine)palladium(0) in toluene (20 mL) was added a suspension of 7 (1.93 g, 4.15 mmol) in ethanol (5.2 mL) and an aqueous solution of K₂CO₃ (765 mg, 5.54 mmol). The mixture was degassed and purged with N₂ for 15 minutes. The mixture was refluxed overnight. After the completion of reaction (TLC), the flask was allowed at cool to room temperature. The mixture was extracted with CH₂Cl₂ and the organic layer was washed with brine, dried with MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (ethyl acetate/hexane 10:90) provided the coupled product 14 in 86% yield. Mp: 110-115 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.12 (s, 12H, -Si(CH₃)₂), 0.13 (s, 12H, -Si(CH₃)₂), 0.18 (s, 12H, -Si(CH₃)₂), 0.96 (s, 18H, -C(CH₃)₃), 0.98 (s, 18H, -C(CH₃)₃), 1.02 (s, 18H, -C(CH₃)₃), 6.42 (d, J = 8.2 Hz, 2H, ArH), 6.58 (d, J = 8.2 Hz, 2H, ArH), 6.68 (d, J = 1.8 Hz, 2H, ArH), 6.79 (s, 2H, ArH). ¹³C NMR (75.45 MHz, CDCl₃, ppm): δ -4.13, -4.07, -4.02, 18.41, 25.93, 120.05, 122.28, 122.93, 123.07, 133.24, 134.88, 145.17, 145.45, 146.11. MS (FAB+) m/z: 1011. Elemental analysis: calcd. for C₅₄H₉₈O₆Si₆: C 64.10, H 9.76; Found: C 64.01, H 9.46.

Synthesis of 2,3,6,7,10,11-hexakis(tert-butyldimethylsilyloxy)triphenylene (14a)

To a solution of hexahydroxy triphenylene (150.0 mg, 0.46 mmol) in DMF (5 mL) was added imidazole (314 mg, 4.62 mmol). The reaction mixture was stirred for 10-15 minutes at room temperature. Then TBDMSCl (699 mg, 4.62 mmol) was added to reaction mixture in portions wise and the mixture was stirred at room temperature overnight. After completion of the reaction (TLC), reaction mixture was extracted with DCM and water. The organic layer was separated out, washed with brine, dried over MgSO₄, and filtered. The filtrate was evaporated to dryness under reduced pressure and column chromatography over silica gel (hexane) was
carried out to give compound 14a in 89% yield. Mp: 125-127 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.30 (s, 36H, -Si(CH$_3$)$_2$), 1.05 (s, 54H, -C(CH$_3$)$_3$), 7.76 (s, 6H, ArH). $^{13}$C NMR δ (75.45 MHz, CDCl$_3$, ppm): δ 4.08, 18.65, 26.02, 113.96, 123.78, 146.60. MS (FAB+) m/z: 1009. Elemental analysis: calcd. for C$_{54}$H$_{96}$O$_6$Si$_6$: C 64.23, H 9.58; Found: C 64.25, H 9.60.

**Synthesis of terphenyl derivative (15)**

To a mixture of 4 (250 mg, 0.84 mmol) and tetrakis(triphenylphosphine)palladium(0) (215 mg, 0.19 mmol) in toluene (10 mL) was added a suspension of 7 (978 mg, 2.11 mmol) in ethanol (3.5 mL) and an aqueous solution of K$_2$CO$_3$ (466 mg, 3.38 mmol). The mixture was degassed and purged with N$_2$ gas for 15 minutes. The mixture was refluxed overnight. After the completion of reaction, the mixture was allowed to cool to room temperature and extracted with dichloromethane (DCM). The organic layer was washed with brine, dried with MgSO$_4$ and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (ethyl acetate/hexane 10:90) provided the coupled product 15 in 79% yield. Mp: 140-142 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.07 (s, 12H, -Si(CH$_3$)$_2$), 0.18 (s, 12H, -Si(CH$_3$)$_2$), 0.93 (s, 18H, -C(CH$_3$)$_3$), 0.98 (s, 18H, -C(CH$_3$)$_3$), 3.92 (s, 6H, -OCH$_3$), 6.56 (d, J = 8.4 Hz, 2H, ArH), 6.63-6.66 (m, 4H, ArH), 6.84 (s, 2H, ArH). $^{13}$C NMR (75.45 MHz, CDCl$_3$, ppm): δ -4.19, -4.07, 18.34, 18.41, 25.89, 25.91, 55.95, 113.62, 120.29, 122.50, 122.78, 132.59, 134.94, 145.41, 146.16, 147.65. MS (ES+) m/z: 811. Elemental analysis: calcd. for C$_{44}$H$_{74}$O$_6$Si$_4$: C 65.13, H 9.19; Found: C 65.19, H 9.39.

**Synthesis of triphenylene-2,3,6,7,10,11-hexao 17a)**

To a stirred solution of 14 (100 mg, 0.09 mmol) in dry THF (2 mL) was added solution of 1M tetra-butylammonium fluoride (TBAF) (194 mg, 0.74 mmol) under aerobic condition, which was accompanied by immediate color change to dark violet. The mixture was stirred at room temperature for 2 hours. After the completion of reaction (TLC), the THF was evaporated and residue was washed with 1M HCl (2 times), chloroform and then treated with excess hexane to get the brown colored solid in 93% yield. Mp: >250 °C. $^1$H NMR (300 MHz, DMSO-d$_6$, ppm): δ 7.58 (s,
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

6H, ArH). $^{13}$C NMR (75.45 MHz, DMSO-$d_6$, ppm): $\delta$ 107.84, 121.90, 145.29. Elemental analysis: calcd. for C$_{18}$H$_{12}$O$_6$: C 66.67, H 3.73; Found: C 66.37, H 3.43.

**Synthesis of 10,11-dimethoxytriphenylene-2,3,6,7-tetraol (17b)**

To a stirred solution of 15 (100 mg, 0.12 mmol) in dry THF (2 mL) was added 1M TBAF (160 mg, 0.62 mmol) under aerobic condition. The mixture was stirred at room temperature for 2 hours and extracted with dichloromethane (DCM). The organic layer was washed with 1M aqueous HCl, water, brine, dried over MgSO$_4$ and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude was crystallised from dichloromethane and ether to get the product in 91% yield. Mp: >250 °C. $^1$H NMR $\delta$ (500 MHz, C$_4$D$_8$O, ppm): $\delta$ 3.97 (s, 6H, -OCH$_3$), 7.70 (s, 2H, ArH), 7.77 (s, 2H, ArH), 7.79 (s, 2H, ArH), 8.10 (s, 2H, -OH), 8.25 (s, 2H, -OH). Elemental analysis: calcd. for C$_{20}$H$_{16}$O$_6$: C 68.18, H 4.58; Found: C 68.02, H 4.39.

**Synthesis of triphenylene-2,3,6,7,10,11-hexayl hexakis(trifluoromethanesulfonate) (18)**

2,3,6,7,10,11-Hexahydroxytriphenylene 17a (90 mg, 0.28 mmol) was added to dry dichloromethane (2.5 mL) and pyridine (0.5 mL, 6.71 mmol) at -20 °C. Trifluoromethanesulphonic anhydride (0.6 mL, 3.31 mmol) was slowly added to the solution. The flask was allowed to warm at room temperature and the mixture was stirred overnight. The reaction was quenched by adding 2N HCl solution. The aqueous layer was extracted with dichloromethane (DCM). The organic layer was separated out, dried over silica gel and concentrated under vacuum to get the crude which was purified by column chromatography (SiO$_2$, ethyl acetate/ hexane 5:95) to give the product 18 in 65% yield. Mp: 175-180 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 8.56 (s, 6H, ArH). $^{13}$C NMR $\delta$ (75.45 MHz, CDCl$_3$, ppm): $\delta$ 113.74, 119.51, 128.93, 140.96. MS (FAB+) m/z: 1116. Elemental analysis: calcd. for C$_{24}$H$_6$F$_{18}$O$_{18}$S$_6$: C 25.81, H 0.54, S 17.23; Found: C 25.50, H 0.51, S 16.98.

**Synthesis of 10,11-dimethoxytriphenylene-2,3,6,7-tetrayl tetrakis(trifluoromethanesulfonate) (19)**

To a stirred solution of 17b (66 mg, 0.18 mmol) in DCM (2 mL) and pyridine (0.4 mL, 4.55 mmol) at -20°C was added trifluoromethanesulphonic anhydride (0.25 mL, 1.49 mmol) drop-
wise and slowly with continuous stirring the reaction mixture. After the complete addition, the flask was allowed to warm to room temperature and solution was stirred overnight. The reaction was then quenched with 2N HCl. The aqueous layer was extracted with dichloromethane (DCM). The organic layer was dried over MgSO₄ and concentrated under vacuum. The crude was purified by column chromatography (SiO₂, ethyl acetate/hexane 15:85) to give the product 19 in 68% yield. Mp: 165-170 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 4.17 (s, 6H, -OCH₃), 7.76 (s, 2H, ArH), 8.47 (s, 2H, ArH), 8.52 (s, 2H, ArH); ¹³C NMR δ (75.45 MHz, CDCl₃, ppm): δ 56.27, 104.51, 116.55, 118.29, 118.99, 120.79, 122.94, 127.21, 130.88, 138.46, 140.13, 151.53. MS (FAB+) m/z: 879. Elemental analysis: calcd. for C₂₄H₁₂F₁₂O₁₄S₄: C 32.73, H 1.37, S 14.57; Found: C 32.38, H 1.45, S 14.45.

**Synthesis of terphenyl derivative (20)**

To a stirred solution of compound 15 (100 mg, 0.28 mmol) in mixture of THF:H₂O (95:5) was added 1 M TBAF dropwise and slowly. The mixture was allowed to stir for 2 hours at room temperature. After the completion of reaction, the solvent was removed completely under the reduced pressure and resulting crude was dissolved in DCM (3 mL) and pyridine (0.6 mL, 6.89 mmol). The reaction mixture was cooled to -20 °C and trifluoromethanesulphonic anhydride (0.25 mL, 1.49 mmol) was added with continues stirring the reaction mixture, keeping the temperature at -20 °C. After the complete addition, the mixture was allowed to warm at room temperature and solution was stirred overnight. The reaction was then quenched with 2N HCl. The aqueous layer was extracted with dichloromethane (DCM). The organic layer was dried over the MgSO₄ and concentrated under vacuum to get the crude which was purified by column chromatography (SiO₂, ethyl acetate/hexane 20:80) to provided the compound 20 in 30% yield. Mp: 156-160°C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.95 (s, 6H, -OCH₃), 6.87 (s, 2H, ArH), 7.10 (s, 2H, ArH), 7.25 (d, J = 5.1 Hz, 2H, ArH), 7.38 (s, 2H, ArH). MS (MALDI-TOF) m/z 881.86 (M)+. Elemental analysis: calcd. for C₂₄H₁₄F₁₂O₁₄S₄: C 32.66, H 1.60; Found: C 32.61, H 1.58.

85
**Synthesis of terphenyl derivative (21a)**

![Image](image_url)

To a mixture of 3 (300 mg, 0.604 mmol) and tetrakis(triphenylphosphine)palladium(0) (280 mg) in toluene (10 mL) was added a suspension of boronic ester 10 (398 mg, 1.51 mmol) in ethanol (6.6 mL) and an aqueous solution of K₂CO₃ (333 mg, 2.41 mmol). The mixture was degassed and purged with N₂ for 15 minutes. The mixture was refluxed overnight. After the completion of reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with dichloromethane (DCM) and the organic layer was washed with brine, dried with MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (ethyl acetate/hexane 5:95) provided the coupled product 21a in 82% yield. Mp: 140-142 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.25 (s, 12H, -Si(CH₃)₂), 1.02 (s, 18H, -C(CH₃)₃), 3.58 (s, 6H, -OCH₃), 3.84 (s, 6H, -OCH₃), 6.53 (d, J = 1.8 Hz, 2H, ArH), 6.68-6.77 (m, 4H, ArH), 6.88 (s, 2H, ArH). ¹³C NMR δ (75.45 MHz, CDCl₃, ppm): δ -4.02, 18.45, 25.95, 55.58, 55.83, 110.79, 113.65, 124.67, 122.79, 133.24, 134.26, 145.81, 147.44, 148.10. MS (FAB+) m/z: 611. Elemental analysis: calcd. for C₃₄H₅₀O₆Si₂: C 66.84, H 8.25; Found: C 66.60, H 8.15.

**Synthesis of terphenyl derivative (21b)**

To a mixture of 4 (648 mg, 2.19 mmol) and tetrakis(triphenylphosphine)palladium(0) (554 mg) in toluene (22 mL) was added a suspension of boronic ester 13a (1.82 g, 5.47 mmol) in ethanol (9.0 mL) and an aqueous solution of K₂CO₃ (1.21 g, 8.78 mmol). The mixture was degassed and purged with N₂ for 15 minutes. The mixture was refluxed overnight. After the completion of reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with dichloromethane (DCM) and the organic layer was washed with brine, dried with MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure. The product 21b was isolated by column chromatography (SiO₂, ethyl acetate/hexane 5:95) as a white solid in 69% yield. Mp: 72-75 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.05 (s, 12H, -Si(CH₃)₂), 0.92 (s, 18H, -C(CH₃)₃), 3.93 (s, 6H, -OCH₃), 6.60-6.62 (m, 2H, ArH), 6.71 (dd, J₁ = 7.8 Hz, J₂ = 7.8 Hz, 4H, ArH), 6.89 (s, 2H, ArH), 7.08 (t, J = 7.8 Hz, 2H, ArH); ¹³C NMR (75.45 MHz, CDCl₃, ppm): δ -4.52, 18.09, 25.63, 56.05,
Synthesis of terphenyl derivative (21c)

To a mixture of 4 (578 mg, 1.95 mmol) and tetrakis(triphenylphosphine)palladium(0) (495 mg) in toluene (20 mL) was added a suspension of boronic ester 13b (1.62 g, 4.87 mmol) in ethanol (8.1 mL) and an aqueous solution of K$_2$CO$_3$ (1.07 g, 7.80 mmol). The mixture was degassed and purged with N$_2$ for 15 minutes. The mixture was refluxed overnight. After the completion of reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with dichloromethane (DCM) and the organic layer was washed with brine, dried with MgSO$_4$ and filtered. The filtrate was evaporated to dryness under reduced pressure. The product was isolated by column chromatography (SiO$_2$, ethyl acetate/hexane 5:95) as a white solid in 73% yield. Mp: 75-80 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.17 (s, 12H, -Si(CH$_3$)$_2$), 0.97 (s, 18H, -C(CH$_3$)$_3$), 3.93 (s, 6H, -OCH$_3$), 6.67 (d, J = 7.8 Hz, 4H, ArH), 6.90 (s, 2H, ArH), 6.95 (s, J = 7.8 Hz, 4H, ArH). $^{13}$C NMR (75.45 MHz, CDCl$_3$, ppm): δ 4.42, 18.22, 25.68, 56.03, 113.51, 119.48, 130.89, 132.68, 134.61, 147.89, 154.13. Elemental analysis: calcd. for C$_{32}$H$_{46}$O$_4$Si$_2$: C 69.77, H 8.42; Found: C 69.73, H 8.49.

Synthesis of terphenyl derivative (22a)

To a stirred solution of 21a (100 mg, 0.16 mmol) in dry THF (2 mL) was added 1M TBAF (171 mg, 0.65 mmol) under aerobic condition. The mixture was stirred at room temperature for 2 hours and extracted with dichloromethane (DCM). The organic layer was washed with 1M aqueous HCl, water, brine, dried over MgSO$_4$ and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude was re-precipitated from dichloromethane and ether. The product was dissolved in dry N,N-dimethylformamide (DMF) and then potassium carbonate (67 mg, 0.49 mmol) was added. The suspension was stirred at room temperature for 5 minutes and then methyl iodide (92 mg, 0.65 mmol) was added drop-wise. The mixture was stirred overnight. After the reaction was completed (TLC), the mixture was poured in water and aqueous layer was extracted with dichloromethane. The organic layer was separated, dried over MgSO$_4$ and concentrated under vacuum to get the crude which was purified by
column chromatography (SiO₂, ethyl acetate/hexane 15:85) to give the pure product in 68% yield. Mp: 105-110°C. ¹H NMR δ (300 MHz, CDCl₃, ppm): δ 3.60 (s, 6H, -OCH₃), 3.85 (s, 6H, -OCH₃), 3.94 (s, 6H, -OCH₃), 6.58 (s, 2H, ArH), 6.77 (d, J = 1.2 Hz, 4H, ArH), 6.94 (s, 2H, ArH). MS (FAB+) m/z: 411. Elemental analysis: calcd. for C₂₄H₂₆O₆: C 70.23, H 6.38. Found: C 70.13, H 6.28.

Synthesis of terphenyl derivative (22b)

To a stirred solution of 21b (100 mg, 0.18 mmol) in dry THF (2 ml) was added 1M TBAF (140 mg, 0.54 mmol) under aerobic condition. The mixture was stirred at room temperature for 2 hours and extracted with dichloromethane (DCM). The organic layer was washed with 1M aqueous HCl, water, brine, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude was re-precipitated from dichloromethane and ether. The product was transferred to dry DCM and pyridine (367 mg, 4.65 mmol) was added. The suspension was cooled down to -20 °C for 5 minutes and then trifluoromethanesulphonic anhydride (209 mg, 0.74 mmol) was added drop-wise. The mixture was stirred overnight. After the reaction was completed (TLC), the mixture was quenched with 2N HCl and aqueous layer was extracted with dichloromethane. The organic layer was separated, dried over MgSO₄ and concentrated under vacuum to get the crude. The product was purified by column chromatography (SiO₂, ethyl acetate/hexane 10:90) as off-white solid in 46% yield. Mp: 85-90 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.96 (s, 6H, -OCH₃), 6.89 (s, 2H, ArH), 6.94-7.35 (m, 8H, ArH). MS (FAB+) m/z: 586. Elemental analysis: calcd. for C₂₂H₁₆F₆O₈S₂: C 45.05, H 2.75; Found: C 44.99, H 2.59.

Synthesis of terphenyl derivative (22c)

To a stirred solution of 21b (100 mg, 0.18 mmol) in dry THF (2 ml) was added 1M TBAF (140 mg, 0.54 mmol) under aerobic condition. The mixture was stirred at room temperature for 2 hours and extracted with dichloromethane (DCM). The organic layer was washed with 1M aqueous HCl, water, brine, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude was re-precipitated from dichloromethane and ether. The product was
transferred to dry DCM and pyridine (367 mg, 4.65 mmol) was added. The suspension was cooled down to -20 °C for 5 minutes and then trifluoromethanesulphonic anhydride (209 mg, 0.74 mmol) was added drop-wise. The mixture was stirred overnight. After the reaction was completed (TLC), the mixture was quenched with 2N HCl and aqueous layer was extracted with dichloromethane. The organic layer was separated, dried over MgSO₄ and concentrated under vacuum to get the crude. The product was purified by column chromatography (SiO₂, ethyl acetate/hexane 10:90) as off-white solid in 42% yield. Mp: 120-125 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.96 (s, 6H, -OCH₃), 6.90 (s, 2H, ArH), 7.11-7.17 (m, 8H, ArH). ¹³C NMR (75.45 MHz, CDCl₃, ppm): δ 56.15, 113.37, 121.01, 131.16, 131.60, 141.33, 148.26, 148.94. MS (FAB+) m/z: 586. Elemental analysis: calcd. for C₂₂H₁₆F₆O₈S₂: C 45.05, H 2.75; Found: C 45.35, H 2.67.

Synthesis of 2,2’-(2,2’-oxybis(ethane-2,1-diyl))bis(ethane-2,1-diyl) bis(4-methylbenzenesulphonate) (24)

Tetraethylene glycol 23 (10 g, 51.48 mmol) and NaOH (6.17 g, 154.44 mmol) were dissolved in 60 mL of 1:1 THF:H₂O mixture and the reaction mixture was cooled at 0 °C. Then a solution of p-toluenesulphonyl chloride (22.0 g, 115.83 mmol) in 32 mL THF was added drop-wise to above solution over 3 hours, maintaining the temperature at 0 °C. the reaction was allowed to stir at room temperature overnight. After the completion of reaction (TLC), reaction mixture was poured into the 100 mL ice cold water and extract with toluene. The organic layer was separated out and treated with solid CaCl₂ to remove any mono product. Finally toluene was removed under reduced pressure to obtain di-tosylate 24 as pale yellow thick oil in 69% yield. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.26 (s, 6H, -CH₃), 3.59-3.62 (m, 12H, crown-H), 4.16 (t, J = 4.8 Hz, 4H, crown-H), 7.33 (d, J = 8.0 Hz, 4H, ArH), 7.79 (d, J = 8.4 Hz, 4H, ArH).

Synthesis of 15,16-dibromo-2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecine (25)

A mixture of 4,5-dibromobenzene-1,2-diol 2 (2.0 g, 7.46 mmol), K₂CO₃ (2.57 g, 18.65 mmol), tetraethyleneglycol ditosylate 24 (5.61 g, 11.19 mmol) and catalytic amount of 18-crown-6 in THF (25 mL) was refluxed for 24 hours. After the completion of reaction (TLC), the solvent was removed under vacumm and residue so obtained was treated with water, extracted with CH₂Cl₂. The organic layer was washed with brine, dried over MgSO₄ and
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

filtered. The filtrate was evaporated to dryness under reduced pressure and compound was purified by chromatography over silica gel (ethyl acetate/hexane 3:7) to give 25 as white solid in 57% yield. Mp: 85-90 °C. 1H NMR (300 MHz, CDCl3, ppm): δ 3.74 (s, 8H, crown-H), 3.89 (t, J = 4.2 Hz, 4H, crown-H), 4.09 (t, J = 4.2 Hz, 4H, crown-H), 7.07 (s, 2H, ArH). 13C NMR (75.45 MHz, CDCl3, ppm): δ 69.2, 69.3, 70.3, 71.0, 115.1, 118.4, 149.0; Elemental analysis: calcd. for C14H18Br2O5: C 39.46, H 4.26; Found: C 39.01, H 4.12.

Synthesis of terphenyl derivative (26)

To a mixture of 25 (0.87 g, 2.05 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.52 g, 0.45 mmol) in toluene (25 mL) was added the suspension of boronic ester 9 (2.19 g, 4.72 mmol) in ethanol (3 mL) and an aqueous solution of K2CO3 (1.13 g, 8.21 mmol). The mixture was degassed and purged with N2 for 15 minutes. The mixture was refluxed overnight. After the completion of reaction (TLC), the flask was allowed to cool at room temperature. The mixture was extracted with CH2Cl2 and the organic layer was washed with brine, dried with MgSO4 and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (ethyl acetate/hexane 30:70) provided the coupled product 26 in 63% yield. Mp: 192-196 °C. 1H NMR (300 MHz, CDCl3, ppm): δ 0.06 (s, 12H, -Si(CH3)2), 0.17 (s, 12H, -Si(CH3)2), 0.93 (s, 18H, -C(CH3)3), 0.97 (s, 18H, -C(CH3)3), 3.77 (s, 8H, crown-H), 3.92 (t, J = 4.3 Hz, 4H, crown-H), 4.18 (t, J = 4.3 Hz, 4H, crown-H), 6.52 (d, J = 8.4 Hz, 2H, ArH), 6.61-6.64 (m, 4H, ArH), 6.82 (s, 2H, ArH). 13C NMR (75.45 MHz, CDCl3, ppm): δ -4.18, -4.07, 18.33, 18.41, 25.91, 69.18, 69.71, 70.62, 71.13, 116.36, 120.26, 122.47, 122.77, 133.23, 134.92, 145.38, 146.13, 147.79. MS (ESI) m/z 941 (M)+. Elemental analysis: calcd. for C50H84O9Si4: C 63.78, H 8.99; Found: C 63.42, H 8.69.

Synthesis of triphenylene derivative (27)

To the stirred solution of 26 (250 mg, 0.26 mmol) in dry THF (5 mL) was added TBAF (319 mg, 1.22 mmol) at room temperature. Resulting mixture was stirred for 2 hours and to this reaction mixture, acylation was carried out in situ by adding lauryl chloride (217 mg, 0.99 mmol), Et3N (0.14 mL, 0.99 mmol) and the catalytic amount of DMAP (15 mg, 0.12 mmol) in dry DCM at 0 °C. After the complete addition, allow the flask to warm at room
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

temperature and solution was stirred overnight. The mixture was extracted with dichloromethane (DCM). The organic layer was dried over the MgSO$_4$ and concentrated under vacuum. The crude was purified by column chromatography (ethylacetate/hexane 30:70) to give the product 27 in 62% yield. Mp: 185-190 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 0.89 (t, J = 6.4 Hz, 12H, -OCOCH$_2$CH$_2$(CH$_2$)$_8$CH$_3$), 1.29 (s, 64H, -OCOCH$_2$CH$_2$(CH$_2$)$_8$CH$_3$), 1.81 (s, 8H, -OCOCH$_2$CH$_2$(CH$_2$)$_8$CH$_3$), 2.64 (t, J = 5.8 Hz, 8H, -OCOCH$_2$CH$_2$(CH$_2$)$_8$CH$_3$), 3.81 (s, 8H, crown-H), 4.03 (s, 4H, crown-H), 4.35 (s, 4H, crown-H), 7.69 (s, 2H, ArH), 8.18 (d, J = 11.4 Hz, 4H, ArH). $^{13}$C NMR δ (75.45 MHz, CDCl$_3$, ppm): δ 14.07, 22.54, 22.64, 29.00, 29.30, 29.38, 29.57, 30.28, 31.87, 35.71, 50.41, 63.42, 108.33, 123.46, 123.85, 135.37, 143.97, 148.01, 150.61. MS (MALDI-TOF) m/z: 1233.7 (M+Na)$^+$. Elemental analysis: calcd. for C$_{74}$H$_{114}$O$_{13}$: C 73.35, H 9.48; Found: C 73.01, H 9.22.

Synthesis of 2,3,13,14-tetrabromo-6,7,9,10,17,18,20,21-octahydrodibenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecine (28)

The dibenzo-18-crown-6 (500 mg, 1.38 mmol) was dissolved in dry DCM (30 mL) and mixture was cooled at 0 °C. Then bromine (1.0 g, 6.25 mmol) was added slowly with continuous stirring the reaction mixture at 0 °C. The reaction mixture was allowed to stir at room temperature overnight. After completion of the reaction (TLC), light yellow colored solid was separated out. The solid was filtered off, washed with excess DCM and dried in vacuum to get the compound 28 as yellow solid in 91% yield. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ 4.18 (t, J = 8.4 Hz, 8H, crown-H), 4.36 (t, J = 8.4 Hz, 8H, crown-H), 6.99 (s, 4H, ArH).

Synthesis of bis-terphenyl derivative (29)

To a mixture of 28 (218 mg, 0.32 mmol) and palladium(0) in toluene (10 mL) was added a suspension of 9 (750 mg, 1.61 mmol) in ethanol (1.1 mL) and 2 M aqueous solution of K$_2$CO$_3$ (356 mg, 2.58 mmol). The mixture was degassed and purged with N$_2$ for 15 minutes. The mixture was refluxed overnight. After the completion of reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with CH$_2$Cl$_2$ and the organic
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

Layer was washed with brine, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (ethylacetate/hexane 15:75) provided the coupled product 29 in 68% yield. Mp: 250-257 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.07 (s, 24H, -Si(CH₃)₂), 0.17 (s, 24H, -Si(CH₃)₂), 0.93 (s, 36H, -C(CH₃)₃), 0.97 (s, 36H, -C(CH₃)₃), 4.04 (s, 8H, crown-H), 4.22 (s, 8H, crown-H), 6.52 (d, J = 8.4 Hz, 4H, ArH), 6.61 (s, 4H, ArH), 6.83 (s, 4H, ArH). ¹³C NMR δ (75.45 MHz, CDCl₃, ppm): δ -4.16, -4.06, 18.34, 18.41, 25.93, 68.97, 69.89, 115.85, 120.27, 122.50, 122.81, 133.08, 134.96, 145.38, 146.14, 147.45. MS (MALDI-TOF) m/z: 1705.9 (M)+. Elemental analysis: calcd. for C₉₂H₁₅₂O₁₄Si₈: C 64.74, H 8.98; Found: C 64.47, H 8.66.

Synthesis of bis-triphenylene derivative (30)

Compound 29 (450 mg, 0.20 mmol) was dissolved in dry THF (8 mL) and 1M TBAF (2.63 mL, 2.63 mmol) was added at room temperature. The mixture was stirred for 2 hours and to this reaction mixture, was added dry DCM (5 mL), Et₃N (0.58 mL, 4.20 mmol) and the catalytic amount of DMAP (64 mg, 0.52 mmol). The resulting mixture was cooled down to 0 °C and lauryl chloride (2.4 mL, 10.55 mmol) was added dropwise and slowly, keeping the temperature at 0 °C. After the complete addition, allow the flask to warm at room temperature and solution was stirred overnight. The mixture was extracted with dichloromethane (DCM). The organic layer was dried over the MgSO₄ and concentrated under vacuum. The crude was purified by column chromatography (ethyl acetate/hexane 40:60) to give the product 30 in 63% yield. Mp: 205-210 °C. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.89 (s, 24H, -OCOCH₂CH₂(CH₂)₈CH₃), 1.29 (s, 128H, -OCOCH₂CH₂(CH₂)₈CH₃), 1.79 (s, 16H, -OCOCH₂CH₂(CH₂)₈CH₃), 2.62 (s, 16H, -OCOCH₂CH₂(CH₂)₈CH₃), 4.12 (s, 8H, crown-H), 4.38 (s, 8H, crown-H), 7.66 (s, 4H, ArH), 8.11 (s, 8H, ArH). ¹³C NMR (75.45 MHz, CDCl₃, ppm): δ 14.06, 22.67, 24.97, 25.01, 29.35, 29.39, 29.56, 29.64, 29.67, 31.91,
Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions

34.19, 34.72, 68.54, 117.38, 117.97, 123.29, 126.63, 128.31, 140.81, 141.70, 149.09, 171.11, 171.31. MS (FAB+) m/z: 2268.37 (M+Na)+. Elemental analysis: calcd. for C\textsubscript{140}H\textsubscript{212}O\textsubscript{22}: C 74.83, H 9.51; Found: C 74.45, H 9.21.

Synthesis of 2,3,6,7,10,11-hexabromotriphenylene (32)

To a solution of triphenylene 31 (300 mg, 1.31 mmol) in nitrobenzene (80 mL) with iron powder (29.4 mg, 0.52 mmol), bromine (1.89 g, 11.84 mmol) was added dropwise over 5 min. The solution was allowed to stir at room temperature for 16 hours. Then reaction was refluxed at 205 °C for 2 hours. The mixture was cooled to room temperature and mixed with excess diethyl ether. The light yellow coloured solid was separated out, washed with fresh diethyl ether. The crude solid was recrystallized from 1,2-dichlorobenzene to give 32 as pale yellow solid in 92% yield. Mp: > 250 °C.

Synthesis of 2,3,6,7,10,11-hexakis(3,4-bis(tert-butyldimethylsilyloxy)phenyl)triphenylene (33)

To a mixture of boronic ester 9 (1.05 g, 2.28 mmol) and tetrakis(triphenylphosphine) palladium(0) (68 mg, 0.06 mmol) in toluene (10 mL) was added a suspension of 2,3,6,7,10,11-hexabromotriphenylene 31 (188 mg, 0.27 mmol) in ethanol (4 mL) and an aqueous solution of potassium carbonate (444 mg, 3.2 mmol). The mixture was refluxed overnight and allowed to cool to room temperature. The mixture was washed with brine, dried over MgSO\textsubscript{4} and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (DCM/hexane 3:5) provided 33 in 81% yield. Mp: 158-161 °C. \(^1\)H NMR δ (300 MHz, CDCl\textsubscript{3}, ppm): δ 0.10 (s, 36H, -Si(CH\textsubscript{3})\textsubscript{2}), 0.21 (s, 36H, -Si(CH\textsubscript{3})\textsubscript{2}), 0.95 (s, 54H, -C(CH\textsubscript{3})\textsubscript{3}), 1.00 (s, 54H, -C(CH\textsubscript{3})\textsubscript{3}), 6.71-6.76 (m, 12H, ArH), 6.84 (d, J = 2.1 Hz, 6H, ArH), 8.56 (s, 6H, ArH). \(^13\)C NMR (75.45 MHz, CDCl\textsubscript{3}, ppm): δ -4.13, -4.02, 18.38, 18.44, 25.96, 29.69, 120.45, 122.64, 122.98, 125.42, 128.51, 135.10, 139.39, 145.87, 146.33. MS (FAB+)
m/z: 2248. Elemental analysis: calcd. for C_{126}H_{204}O_{12}Si_{12}: C 67.32, H 9.15; Found: C 67.74, H 9.03.

**Synthesis of supertriphenylene (34)**

To a stirred solution of 33 (250 mg, 0.11 mmol) in dry THF (8 mL) was added 1M TBAF (435 mg, 1.65 mmol) under aerobic condition. The mixture was stirred at room temperature for 2 hours and extracted with dichloromethane (DCM). The organic layer was washed with 1M HCl, water, brine, dried over the MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude was dissolved in DCM (0.5 mL) and pyridine (0.17 mL) and trifluoromethanesulphonic anhydride (0.18 mL, 1.10 mmol) was added drop-wise and slowly at -20 °C with continuous stirring the reaction mixture. After the complete addition, allow the flask to warm at room temperature and solution was stirred overnight. The reaction was then quenched with 2N HCl. The aqueous layer was extracted with dichloromethane (DCM). The organic layer was dried over the MgSO₄ and concentrated under vacuum. The crude was purified by column chromatography (SiO₂, DCM/Hexane 7:3) to give the supertriphenylene 34 in 72% yield. Mp: 200-204 °C. ¹H NMR (300 MHz, Acetone-d₆, ppm): δ 8.58 (s, 6H, ArH), 9.12 (s, 6H, ArH), 9.92 (s, 6H, ArH); ¹³C NMR (75.45 MHz, d₆-Acetone, ppm): δ 117.60, 121.91, 122.66, 129.50, 130.66, 131.74, 133.04, 140.94, 141.36. MS (FAB+) m/z: 2456 (M)⁺. Elemental analysis: calcd. for C_{66}H_{18}F_{36}O_{36}S_{12}: C 32.28, H 0.74; Found: C 32.16, H 0.71.

2.5. **References**

Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for Fluoride ions


15 (a) Riggs, B. L. Bone and Mineral Research; Annual 2; Elseiver: Amsterdam, 1984; p 366.


