

Summary

Among discotics, triphenylenes have attracted great attention in the field of supramolecular and material chemistry owing to their role as liquid crystalline materials, molecular scale devices and molecular receptors. They are potential components for organic and optoelectronic devices. Triphenylenes as central core for discotic liquid crystals (DLCs) have been extensively studied for their various physical properties including one-dimensional charge migration, one-dimensional energy migration, electroluminescence, ferroelectric switching and alignment and self assembling behaviour on surfaces. Most of the triphenylene derivatives are thermally and chemically stable, their chemistry is fairly accessible and they show a variety of mesophases having interesting electronic properties.

Keeping in view the significance of discotic molecules in material chemistry and supramolecular chemistry we have designed and synthesized a variety of triphenylene based derivatives and studied their self-assembly and photophysical behaviour. We also explored the host-guest chemistry of these derivatives in the presence of different analytes.

For the convenience of the presentation, the results of our finding have been divided into three chapters.

Chapter 1: Introduction and review of literature

Chapter 2: Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for fluoride ions

Chapter 3: Triphenylene derivatives: Synthesis, self-assembly and sensing applications

Chapter 1: Introduction and review of literature

This chapter deals with the introduction and review of literature about the different types of terphenyl and triphenylene based discoidal materials. From the detailed literature review, the following conclusions were drawn:

- ❖ Polyphenyls like terphenyls and triphenylene derivatives have attracted growing interest in the material chemistry owing to their role as liquid crystalline materials and molecular scale devices.
- ❖ A number of triphenylene derivatives are potential components for organic and optoelectronic devices such as one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, field effect transistors, gas sensors etc.

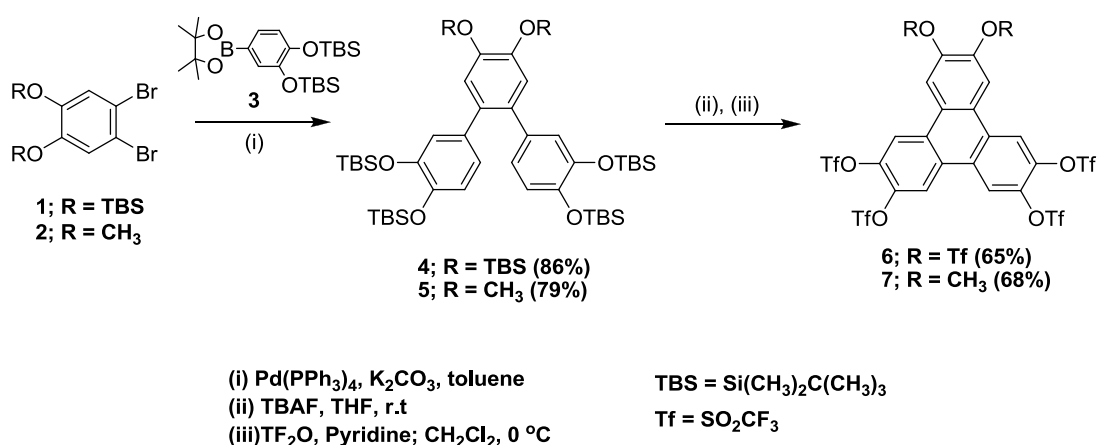
- ❖ Presence of functionalizable groups at the periphery of these derivatives help in fine tuning of these materials and presence of long alkyl chains increases their processibility.
- ❖ Most of the discotic molecules form stable columnar mesophase through π - π interactions among the aromatic cores. The presence of large aromatic cores and intermolecular hydrogen bonding enhances the stability of columnar mesophase.
- ❖ The discotic molecules form stable organogels in non-polar solvents due to the self-assembly. Triphenylene based organogelators have attracted great attention in the field of materials chemistry because they are promising candidates for photo- and electrochemical materials.
- ❖ There are few reports on triphenylene based liquid crystals which show liquid crystalline behavior at room temperature.
- ❖ Although triphenylene derivatives have wide applications in material chemistry, some of them also show sensing applications.

Chapter 2: Synthesis of triphenylene derivatives using fluoride-induced cyclization: Chemodosimeters for fluoride ions.

Triphenylenes derivatives have great potential in supramolecular and material chemistry owing to their role as liquid crystalline materials, molecular scale devices and molecular receptors. However, the synthesis of triphenylenes from terphenyls on a large scale using the conventional oxidizing agents (like FeCl_3) is inconvenient due to the lower solubility of these reagents in the most common organic solvents. In the present chapter, we developed a simple strategy in which terphenyl derivatives having *tert*-butyldimethylsilyloxy groups (-OTBS) undergo fluoride-induced cyclization smoothly without using any oxidizing agents to give symmetrically and unsymmetrically substituted triphenylene derivatives.

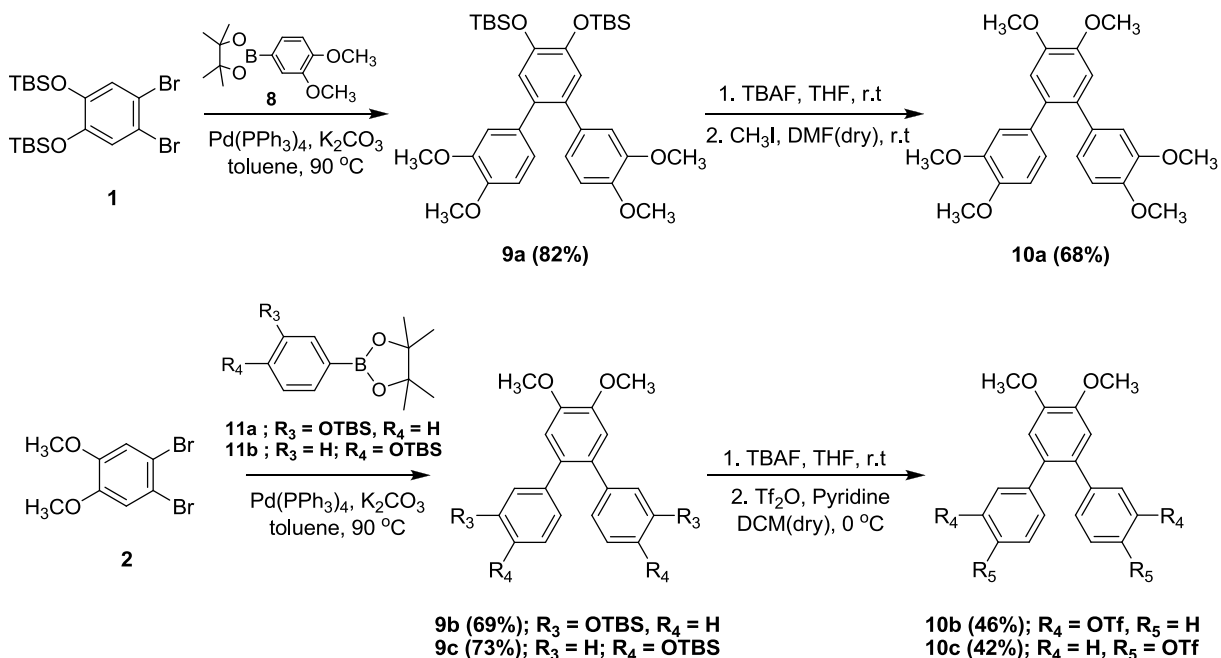
Palladium(0) catalyzed Suzuki-Miyura cross coupling of boronic ester **3** with di-bromo derivatives **1** and **2** furnished terphenyls **4** and **5** in 86% and 79% yields, respectively (**Scheme 2.1**). In the next step, we carried out the deprotection of terphenyls **4** and **5** using tetrabutylammonium fluoride (TBAF). Interestingly, the treatment of terphenyl derivatives **4** and **5** followed by reaction with triflic anhydride furnished symmetrically and unsymmetrically substituted triphenylene derivatives **6** and **7** in 65% and 68% yields, respectively. To gain deeper insight into mechanism of the cyclization reaction, we also prepared a number of terphenyl derivatives **9a-c** (**Scheme 2.2**) using the same synthetic

methodology as that employed for terphenyls **4** and **5** and carried out their deprotection using TBAF.



Scheme 2.1

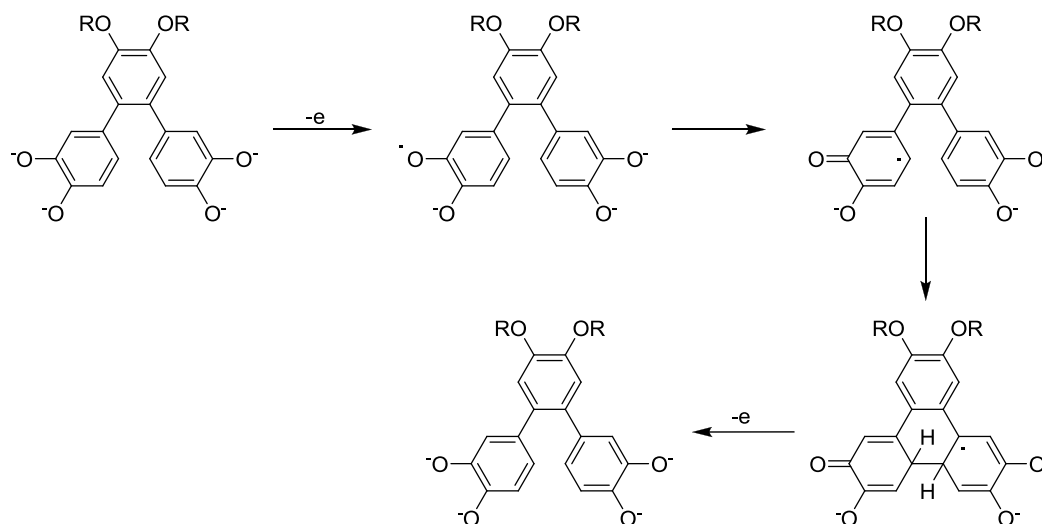
Interestingly, during the deprotection of **9a-c** to **10a-c** using TBAF, no aryl-aryl bond formation was observed as observed in case of compound **4** and **5**. On the basis of these results, we may conclude that increased negative charge on phenolate oxygens after deprotection of -OTBS groups in terphenyls **4** and **5** provide an optimal amount of directing ability and electron density to complete cyclization.



Scheme 2.2

The cyclization is also enthalpically favoured by the greater 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 2.3**.

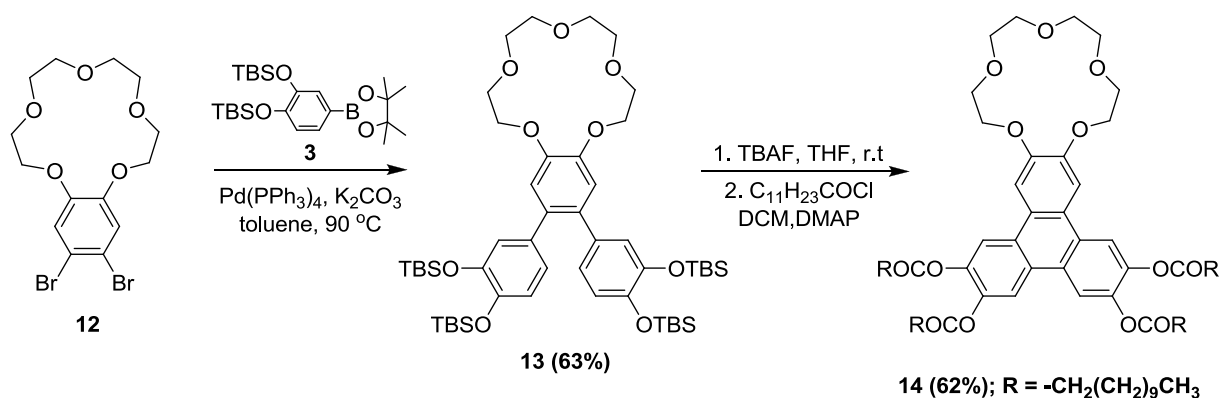


Scheme 2.3

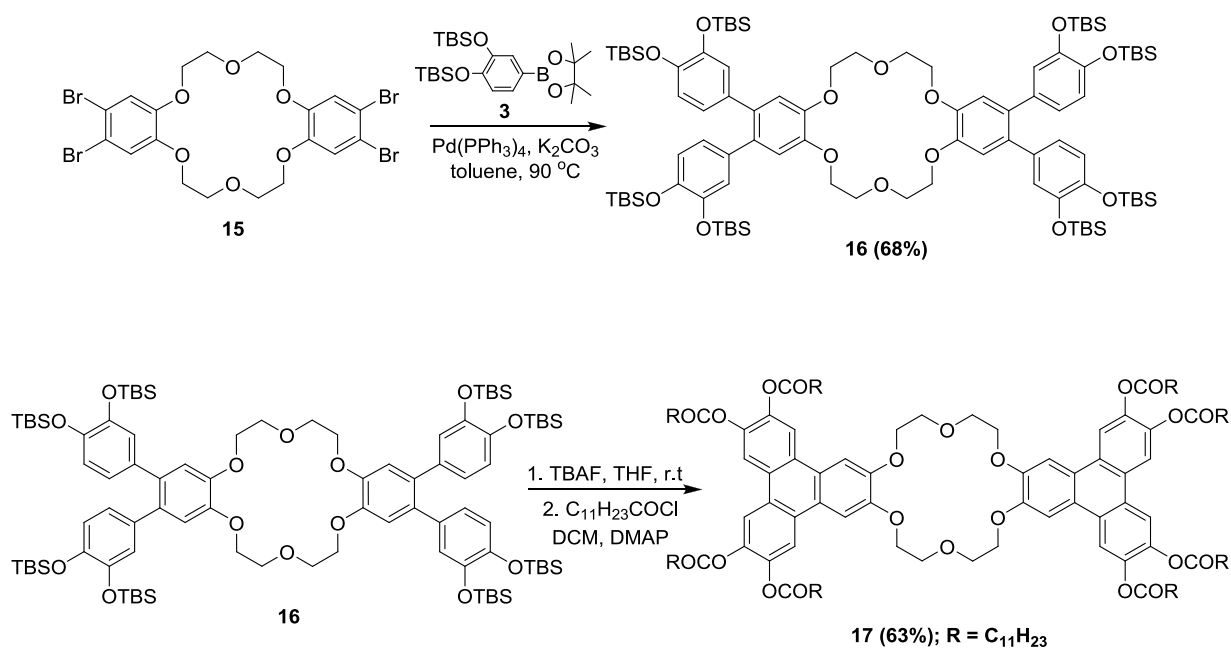
Since the cyclization of terphenyl **4** in the presence of fluoride ions was accompanied by drastic colour changes, we examined the behaviour of terphenyls **4** and **5** toward different anions by UV-vis and fluorescence spectroscopy. Among the various anions such as Cl^- , Br^- , I^- , SO_4^{2-} , OAc^- , HPO_4^- , NO_3^- , and H_2PO_4^- , compounds **4** and **5** act as highly selective chemodosimeters for F^- ions.

Recently, design and synthesis of discotic mesogens carrying crown ether moiety has attracted greater 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 is inconvenient as ether hydrolysis is a known side reaction in 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 that conversion of less than 5% was achieved after 4 weeks irradiation. Using the same synthetic methodology as used for the synthesis of **6** and **7**, we synthesized crown-ether linked triphenylene derivatives **14** and **17**. Palladium(0) catalyzed Suzuki-Miyaura cross coupling between compound **12** and boronic ester **3** furnished terphenyl derivative **13** in 63% yield as shown in **Scheme 2.4**. We then adopted a two step

one pot strategy wherein deprotection of derivative **13** using TBAF in dry THF and subsequent reaction with lauryl chloride furnished compound **14** in 62% yield. We synthesized bis-terphenyl derivative **16** by Suzuki-Miyaura cross coupling of bromo derivative **15** with boronic ester **3** in 68% yield (Scheme 2.5). Deprotection of derivative **16** using TBAF and its subsequent reaction with lauryl chloride yielded triphenylene derivative **17** in 63% yields.



Scheme 2.4

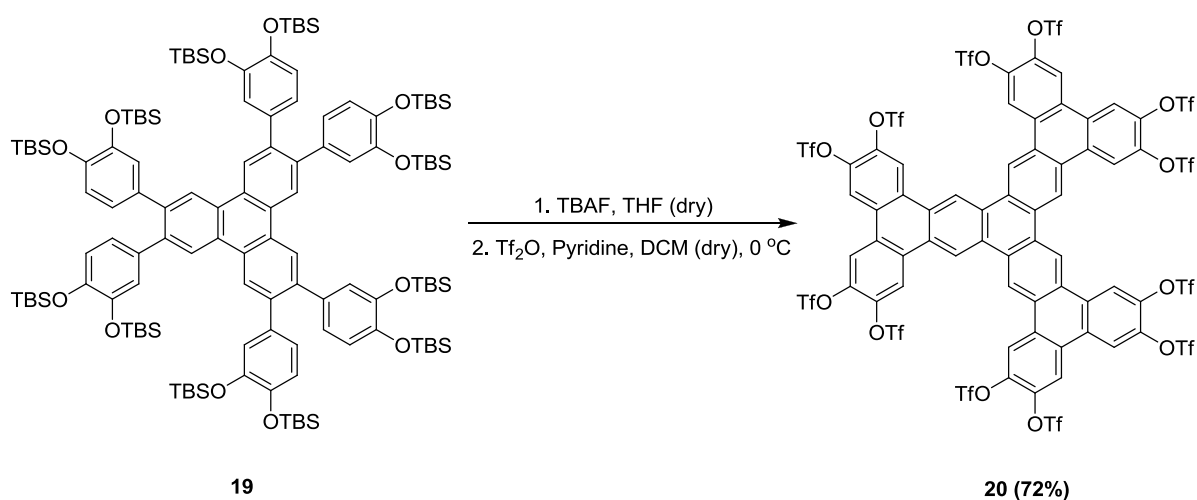
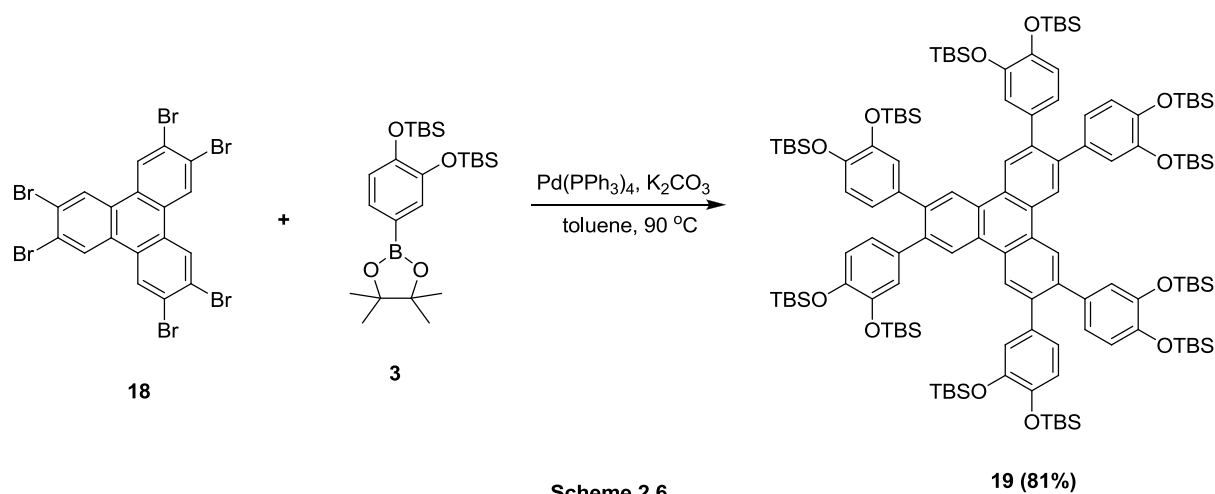


Scheme 2.5

UV-vis and fluorescence studies showed that both derivatives **13** and **16** act as highly selective and sensitive chemodosimeters for the F⁻ ions over the other anions tested. Further the compound **17** formed organogel in non-polar solvent like cyclohexane which was investigated by polarized optical microscope (POM) and scanning electron microscope

(SEM). Upon cooling from isotropic phase it showed an irregular texture with small grains down to the room temperature.

In continuation of this work, we also synthesized extended triphenylene derivative **19** having large core size as the presence of larger aromatic core influences the mesomorphic properties of discotic liquid crystals. They form columnar mesophase which have high mobilities along the axis of column. The synthesis of derivative **19** involves the palladium catalyzed Suzuki-Miyura cross coupling of hexabromotriphenylene **18** with boronic ester **3** (Scheme 2.6).



Further, the treatment of extended triphenylene derivative **19** with tetrabutylammonium fluoride and its subsequent reaction with triflic anhydride furnished supertriphenylene **20** in 72% yield, where three C-C bonds are formed in single step (Scheme 2.7). Both UV-vis studies and fluorescence studies indicate that derivative **19** is highly selective for the F⁻ ions over the other anions with detection limit of 8×10^{-7} M which is sufficiently low for the detection of submillimolar concentration range of F⁻ ions found in many chemical systems.

Chapter 3: Triphenylene derivatives: Synthesis, self-assembly and sensing applications.

In this chapter, we have designed and synthesized triphenylene derivatives having triazole and urea moieties and studied their self-assembly behaviour and sensing applications towards the different analytes (anions, cations and neutral species). For the convenience of presentation, this chapter has been divided into three sections and are discussed as follow

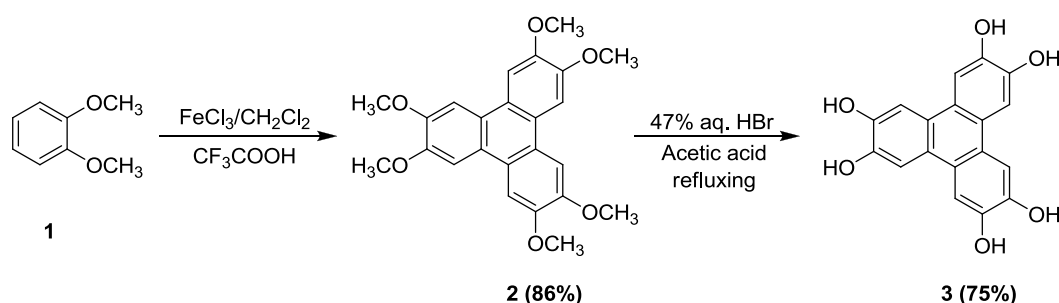
3.1. Triazole modified symmetrically substituted triphenylene derivatives: Synthesis and self-assembly

3.2. Triphenylene based copper ensemble for the detection of cyanide ions

3.3. Triphenylene derivatives: Chemosensors for sensitive detection of nitroaromatic explosives

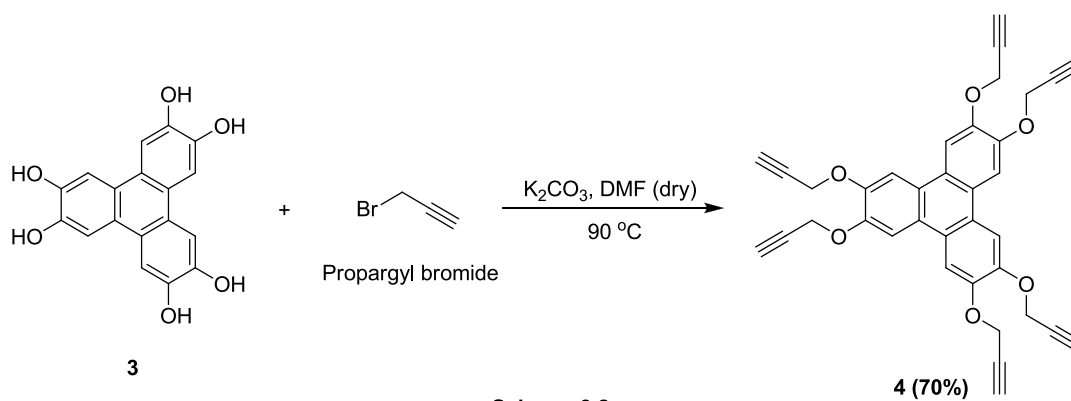
3.1. Triazole modified symmetrically substituted triphenylene derivatives: Synthesis and self-assembly

Among discotics, the triphenylene (TP) derivatives have been widely studied for their liquid crystalline behaviour. In literature there are a few triphenylene derivatives reported which show liquid crystalline behaviour at room temperature. In the present sections we have designed and synthesized the symmetrically substituted triphenylene derivatives having triazole moieties using “click chemistry” These derivatives showed columnar mesophase over a wide range and formed supramolecular aggregates both in bulk and in solution phases. The columnar assembly of TP moiety is further stabilized down to room temperature due to dipole-dipole interactions among 1,2,3-triazole groups. The deprotection of 2,3,6,7,10,11-hexamethoxytriphenylene **2** was carried out by refluxing the solution of **2** in 47% HBr and acetic acid under nitrogen to furnish the 2,3,6,7,10,11-hexahydroxytriphenylene **3** as grey colored solid in 75% yield (**Scheme 3.1**).

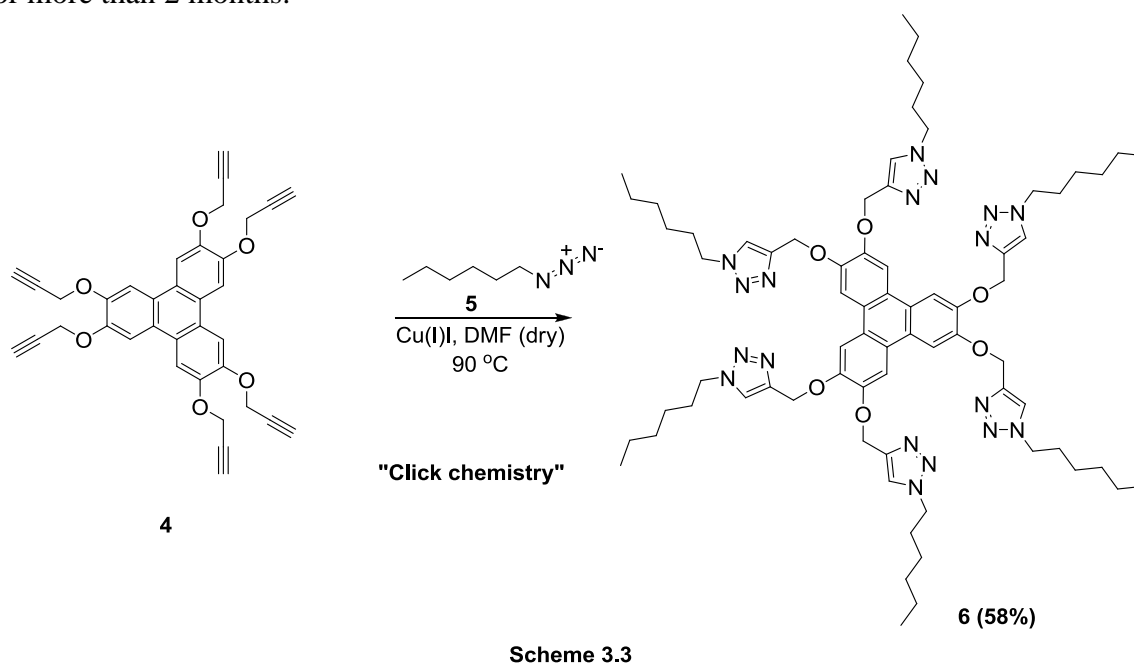


Scheme 3.1

The alkylation of 2,3,6,7,10,11-hexahydroxytriphenylene **3** with propargyl bromide in dry DMF gave 2,3,6,7,10,11-hexakis(prop-2-ynyloxy)triphenylene **4** in 70% yield (**Scheme 3.2**).

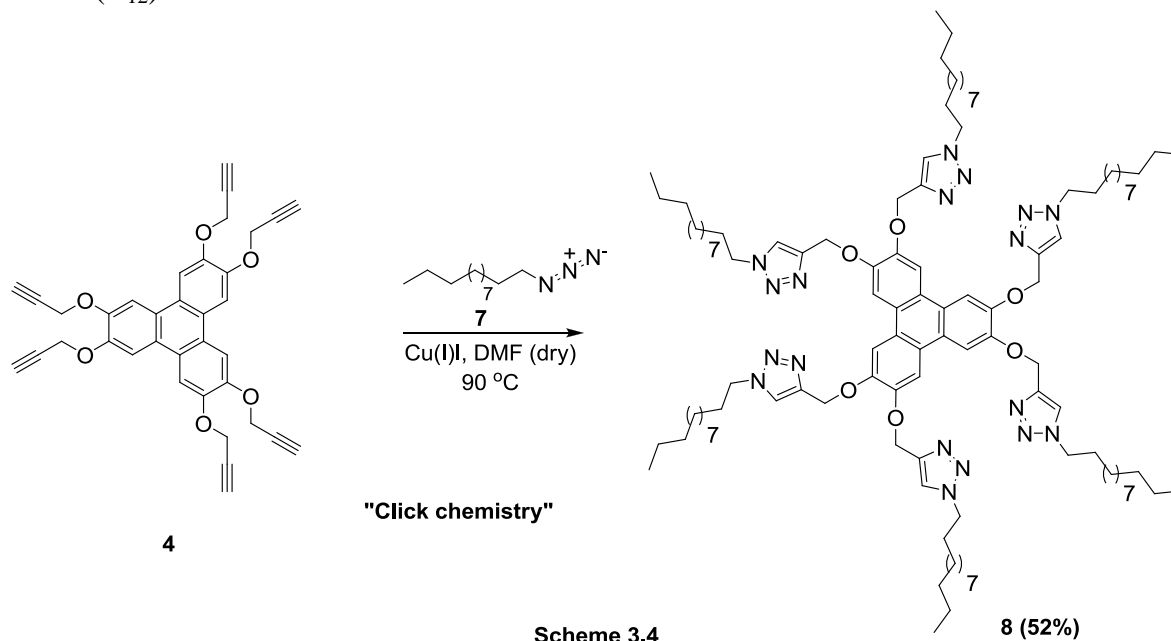


The final discotic molecule **6** was synthesized by Cu-catalyzed “click reaction” of precursor **4** with 1-azidohexane **5** in dry DMF in 58% yield (**Scheme 3.3**). The derivative **6** showed self-assembly behaviour in bulk and solution phase which was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (POM), powder X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Compound **6** formed thermoreversible organogels in cyclohexane and mixed solvents such as hexane and dichloromethane (4:1) that was stable for more than 2 months.



Thermal stability of the gel was measured by the dropping-ball method. The gel stability was tested by the influence of Cd^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} ions as their perchlorate salt. Interestingly, with progressive addition of 10 equiv. of these cations, only gel phase treated with Cd^{2+} ions was transformed into sol phase and in presence of Ni^{2+} , Cu^{2+} , and Hg^{2+} ions, weakening of the gel phase was observed. Further to study the effect of chain length on self-

assembly behaviour, we synthesized triazole-modified triphenylene derivative **8** with long chains (C_{12}) as shown in **Scheme 3.4**.

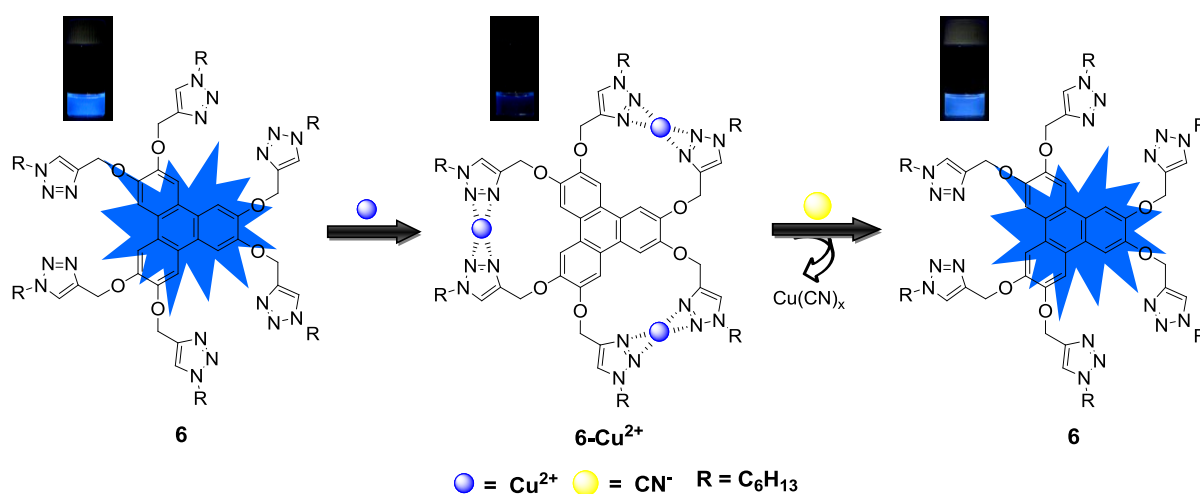


The thermal stability and self-assembly behaviour of derivative **8** was studied by combination of DSC, TGA, POM and SEM analysis. Further, derivative **8** also showed gelation behaviour in non-polar solvents like cyclohexane and DCM:Hexane (1:4) mixture. However in this case, the high concentration (3.5 mg) of gelator **8** was required in contrast to derivative **6** (2.5 mg) for the formation of gel and corresponding T_{gel} was only 39°C. So it indicated that derivative **8** showed weak self-assembly as compared to derivative **6**.

3.2. Triphenylene based copper ensemble for the detection of cyanide ions

Due to high fluorescence intensity of derivative **6** in DMSO and the presence of six triazole groups, we investigated its binding behaviour toward different metal ions as triazole moieties can provide multi-dentate metal coordination sites. In UV-vis spectra, addition of Cu^{2+} ions (0-50 equiv.) resulted in increase in absorption intensity of band at 309 nm, thus indicating interaction between derivative **6** and Cu^{2+} ions. The fluorescence spectra of **6** (2.5×10^{-6} M) in DMSO exhibited an emission band at λ_{max} 384 nm with two shoulders at 374 and 404 nm (excitation 275 nm). Upon addition of incremental amounts of Cu^{2+} ions (0-250 equiv.) to the solution of **6** in DMSO, complete quenching of emission band at 384 nm was observed. The Stern-Volmer plot showed the linear dependence of fluorescence intensity ratio (I/I_0) on the concentration of Cu^{2+} ions added. Since cyanide ions co-ordinate with Cu^{2+} ions to form a very stable complex $Cu(CN)_x$, we studied the sensing behaviour of **6**- Cu^{2+} ensemble towards the different anions by using UV-vis. and fluorescence studies. Interestingly, with gradual

addition of tetrabutylammonium cyanide (TBACN) to **6-Cu²⁺** ensemble, complete recovery of absorption bands corresponding to the free receptor **6** was observed. Similarly, in fluorescence spectra, the completely quenched fluorescence of **6** in DMSO by Cu²⁺ was turned on after addition of CN⁻, at concentrations as low as 2.5×10^{-6} M, thus, indicating demetallation of **6-Cu²⁺** ensemble. We propose that in presence of Cu²⁺ ions, derivative **6** formed non-fluorescent **6-Cu²⁺** complex however, in presence of cyanide ions demetallation of **6-Cu²⁺** complex takes place due to formation of stable [Cu(CN)_x]ⁿ⁻ species which restores the original absorption and emission of derivative **6** (Scheme 3.5).



Scheme 3.5

Keeping in view the importance of cyanide sensing in water and in the presence of chloride and/or phosphate ions, we performed the sensing experiment in a plasma-like aqueous solution containing bovine serum albumin (PLAS: 0.1 M Cl⁻, 2 mM HPO₄²⁻, 0.1 M Na⁺, 4 mM K⁺, pH = 7.4, 46g/l BSA pH = 7.4). The ensemble **6-Cu²⁺** in presence of CN⁻ ions showed similar sensing behaviour with plasma as was observed in the solution without plasma with detection limit of 5.93×10^{-6} M. Biological applicability of **6-Cu²⁺** ensemble to CN⁻ was checked by carrying out fluorescence titrations by taking an *in situ* prepared Cu²⁺ complex and titrating this by varying the concentrations of blood serum. No change was observed in the fluorescence intensity of ensemble **6-Cu²⁺** in presence of serum.

3.3. Triphenylene derivatives: Chemosensors for sensitive detection of nitroaromatic explosives

1. Triazole modified triphenylene based derivatives for the detection of nitroaromatic explosives
2. Extended triphenylene based derivative having urea moieties for the detection of nitroaromatic explosives

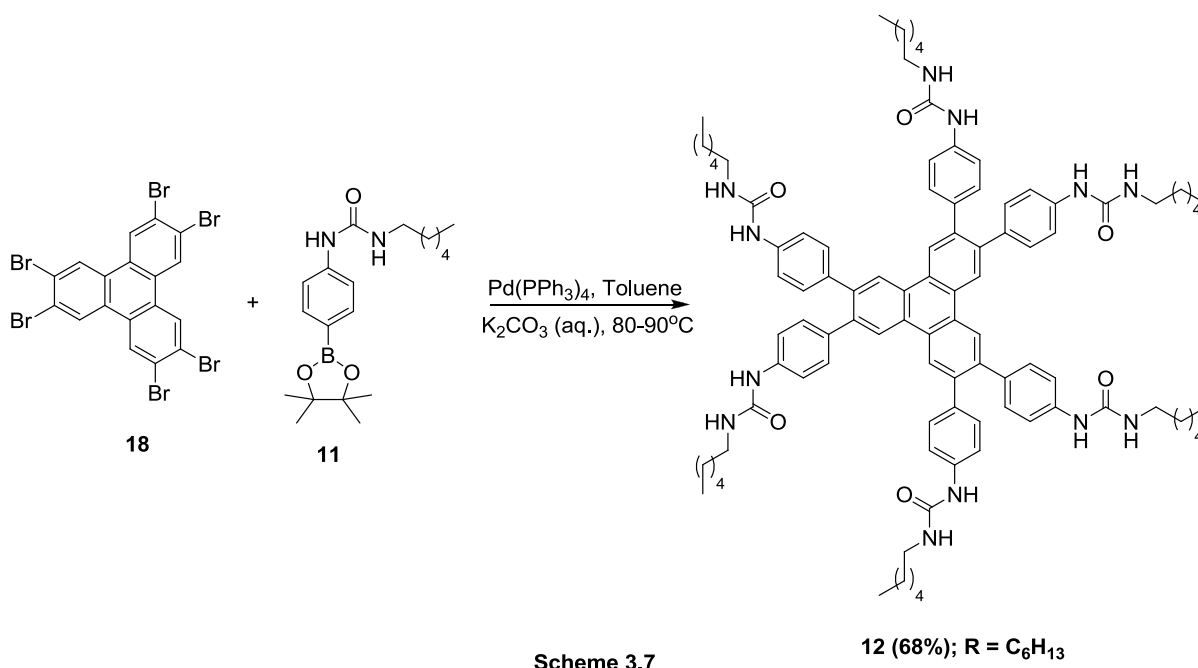
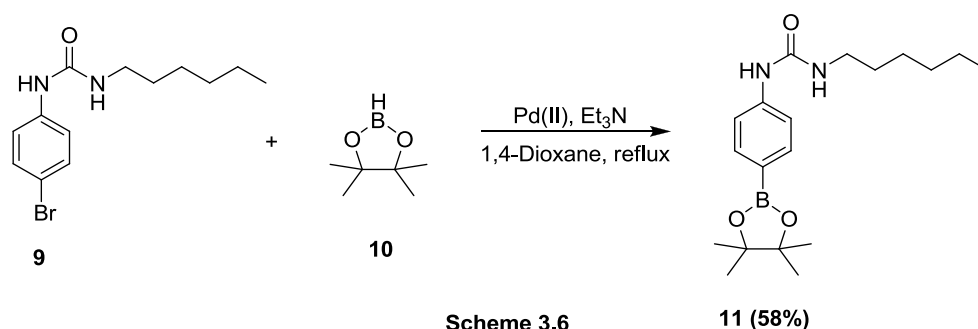
3.3.1. Triazole modified triphenylene based derivatives for the detection of nitroaromatic explosives

Due to the high fluorescence intensity and electron rich nature, we investigated the behaviour of compound **6** for sensing of nitroaromatic compounds (NAC) such as 1,4-dinitrotoluene (DNT), 1,4-dinitrobenzene (DNB), Picric acid (PA), nitrotoluene (NT) and benzoquinones (BQ). The fluorescence spectrum of **6** (5.0×10^{-7} M) in DMSO exhibited an emission band at λ_{max} 383 nm with two shoulders at 371 and 403 nm when excited at 278 nm. Upon addition of picric acid (270 equiv), the fluorescence emission was completely quenched. The quenching of fluorescence was also observed with of DNB (500 equiv), DNT (520 equiv), NT (650 equiv) and BQ (5000 equiv). For vapour phase detection of nitroaromatics, we exposed organogel of derivative **6** in cyclohexane to vapors of picric acid by inserting the vial containing organogel into a sealed vial at room temperature containing solid picric acid and cotton gauze, which prevents direct gel-analyte contact and helps to maintain a constant vapor pressure. The complete gel to sol transition was observed in 8 h with quenching of the fluorescence. The SEM images of sol showed presence of nano-rod like structures due to the collapsing of the nanostructures in the presence of picric acid.

Similarly, we explore the potential applications of derivative **8** as chemosensor for the detection of nitroaromatics. It showed emission at 384 nm when excited at 275 nm. Upon the incremental addition of picric acid (0 to 30 equiv), quenching in the fluorescence was observed. We believe that though derivative **8** does not form gel in the solvent mixture of H₂O:THF (0.5:9.5) due to the weak π - π interactions between the molecules yet its molecules have ordered organisation enabling long range exciton migration and their quick annihilation by the explosive quenchers. To study the practical applications of derivative **8**, we carried out the vapour phase detection of picric acid by preparing the test strips by dipping them in hot gel solutions of derivative **8** followed by drying them under vacuum. PA crystals were placed over a test strip for 5 seconds. Upon illumination with UV lamp, black spots were observed in the contact area. For detection of very small amounts of PA, we prepared the aqueous solution of PA of different concentration and 6 μ L of each solution was placed on the gel coated test strips. The minimum amount of PA, detectable by naked eye was in the nanomolar range. The quenching in the fluorescence intensity was also observed by the use of much higher concentration of other nitroaromatic compounds such as NT (75 equiv.), DNB (80 equiv.), DNT (110 equiv.), TNT (140 equiv.), NB (135 equiv.).

3.3.2. Extended triphenylene based derivative having urea moieties for the detection of nitroaromatic explosives

In the present section we have design and synthesized new electron rich extended triphenylene derivative **12** having urea moieties for both chromogenic and fluorogenic detection of these nitroaromatic compounds. The boronic ester of urea derivative **11** was prepared in 58% yield by carrying out reaction of bromo derivative **9** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane **10** in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ as catalyst (**Scheme 3.6**).



Palladium(0) catalyzed Suzuki-Miyaura cross coupling of boronic ester **11** with hexabromotriphenylene **18** furnished extended triphenylene derivative **12** in 68% yields (**Scheme 3.7**). Compound **12** is highly fluorescent in solution as it exhibited strong emission band at 422 nm in $\text{H}_2\text{O}:\text{DMSO}$ (2:8) mixture. The strong emission of derivative **12** prompted us to use it as sensory materials for detection of different NAC's such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), picric acid (PA), 1,4-dinitrobenzene (DNB), nitromethane

(NM), nitrotoluene (NT), 2,3-dimethyl-2,3-dinitrobutane (DMDNB) and electron deficient 1,4-benzoquinone (BQ) by fluorescence spectroscopy. Fluorescence studies of compound **12** were carried out in H₂O:DMSO (2:8) mixture at 1×10^{-6} M concentration. Upon addition of incremental amount of PA (50 equiv.), quenching of emission band at 422 nm was observed. The emission response of derivative **12** to PA with its increasing concentrations was studied by Stern-Volmer plot which was found to be linear at lower concentration, indicating that fluorescence quenching involves the static quenching mechanism but at higher concentration the plot was found to be hyperbolic curved which may be due to the combination of both static and dynamic (collision) quenching. The quenching in fluorescence emission was also observed upon the addition of 120 equiv. of TNT under similar set of conditions. Further, the UV-vis spectrum of compound **12** in H₂O:DMSO (2:8) was characterized by the presence of one absorption maximum peak at 320 nm. Upon the addition of increasing amounts of TNT (0-20 equiv.) to the solution of **12** in H₂O:DMSO (2:8) mixture, increase in intensity of absorption band at 320 nm was observed with the formation of a new band at 532 nm which goes on increasing upto the addition of 20 equiv of TNT. These spectral changes were also accompanied by colour change from colourless to light pink, visible to naked eye thus, suggesting charge-transfer interaction between **12** and TNT. The fluorescence quenching was also observed with addition of other nitroaromatics such as DNB (130 equiv.), DNT (150 equiv.), NT (175 equiv.) and BQ (480 equiv.), whereas no significant fluorescence quenching was observed with NM and DMNB.

Further to check the practical applicability of compound **12**, we performed the test strip method in contact mode in which fluorescence quenching was observed upon dipping the test strips into a solution of PA (10^{-3} M) and TNT (10^{-3} M). For the visual detection of TNT, small spots of different concentrations of TNT were applied on solution coated test strips. Development of coloured spots of different intensity was observed, which shows that the regulation of the quenching behaviour of TNT is also practically applicable by varying the concentration of TNT.

Thus, the present work deals with synthesis of various triphenylene based discoidal materials and evaluation of their self-assembly behaviour and sensing applications toward various analytes (cations, anions and nitroaromatic explosives).