

Synopsis

entitled

**Self-assembly of Renewable Nano Glycyrrhetic and
Arjunolic acids: Visual Detection of Nitroaromatics by
Arjunolic acid Derivatives**

For the degree of

Doctor of Philosophy in Chemistry

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Thesis Abstract

Spontaneous self-assembly of molecules and ions in aqueous and non-aqueous media leading to various types of supramolecular architectures such as vesicles, fibers, spheres, tubules etc. of nano to micrometer dimensions and gels has become an area of an immense interest in recent years for an improved understanding of the self-assembly process in a medium and also because of their tremendous potential and realized technological applications. **Chapter I** gives an overview on self-assembly and gels.

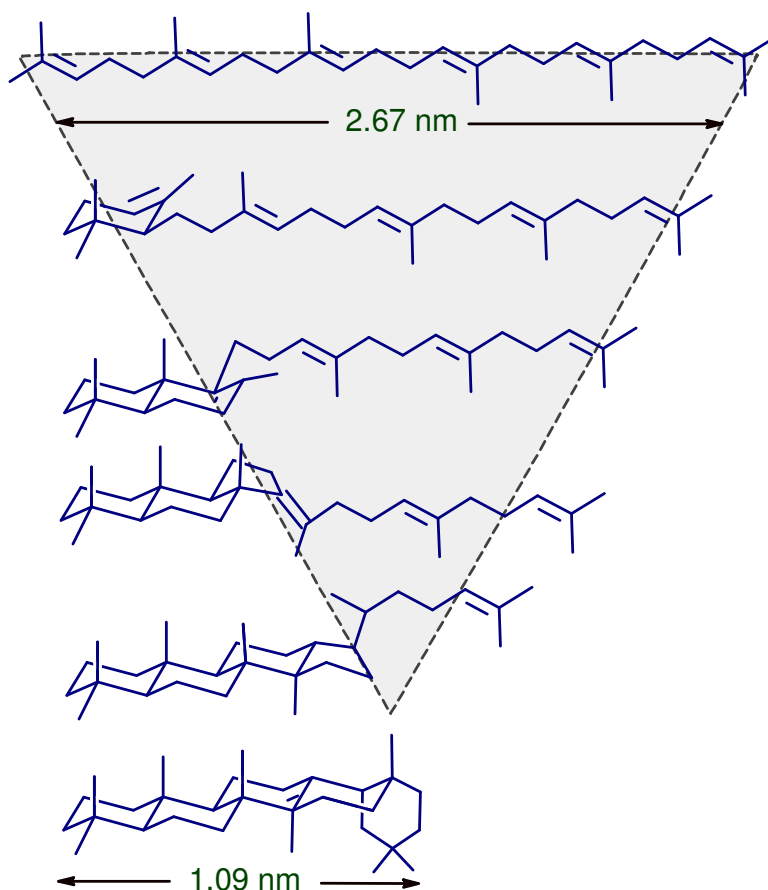


Figure 1: A schematic representation of the variation of the lengths of the triterpenoids with the number of the fused rings.

There has been a tremendous research interest in recent years on the utilization of plant based chemicals as renewables because such a strategy will facilitate continual supply of the raw materials thereby preventing the fast depletion of non-renewable feed-stocks (including petroleum). Plant secondary metabolites, many of which are structurally very complicated, are very attractive candidates as new LMOGs because they are available in renewable supply without extensive synthetic effort. One important class of these metabolites is triterpenoids consisting of 30 carbon atoms having several chiral centers and different functional groups at different positions and orientations. These structural features of the triterpenoids make them an attractive candidate as supramolecular building blocks. Since triterpenoids have diversified backbones with different ring systems, we were curious to know their molecular lengths before utilizing them as supramolecular building blocks. **Chapter II** describes detailed computations with sixty naturally occurring triterpenoids having acyclic and mono-cyclic to fused pentacyclic backbones. Interestingly, force-field calculations revealed that all the triterpenoids are of nano-metric lengths with varied rigid and flexible parts. Monte-Carlo investigation of their conformational space revealed that the nanometric lengths are maintained even in the folded conformers rendering all the triterpenoids useful as renewable nano-sized building blocks. These frameworks can also be used for developing diverse building blocks with a wide variety of structural modifications which are capable of forming supramolecular nano to micro architectures.

Chapter III describes the extraction of a nano-sized triterpenoid *18 β -glycyrrhetic acid* from the root of the medicinal plant *Glycyrrhiza glabra* and its self assembly properties in different liquids. *18 β -glycyrrhetic acid* is a 6-6-6-6-6

pentacyclic mono hydroxy triterpenic acid having an enone moiety in the C ring. The molecule is an excellent gelator of a wide range of organic liquids yielding thermo-reversible gels. Morphological studies revealed the formation of mostly nano to micro-sized spherical and flower like objects consisting of fibrillar networks having fibers of nanometer diameters. The self-assemblies have been utilized for the templated growth of CdS nanoparticles.

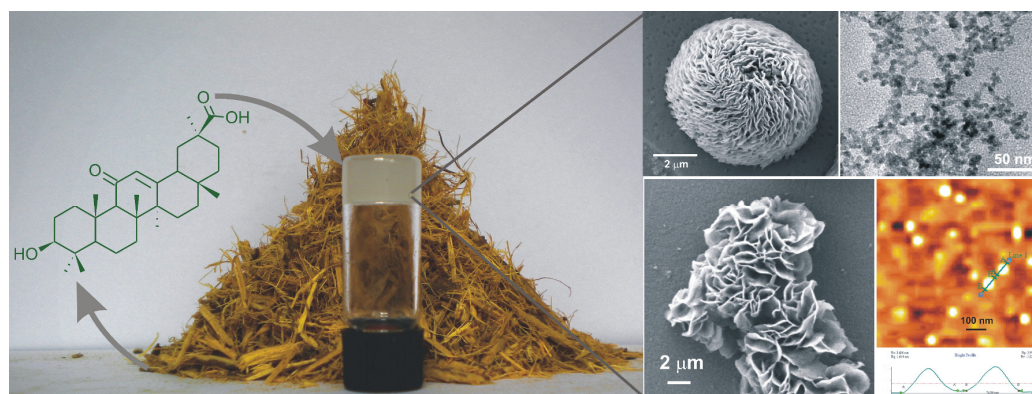


Figure 2: Schematic representation of self-assembly of 18β -glycyrrhetic acid affording spherical and flower-like objects yielding a gel. The inverted vial contains a gel with crushed *Glycyrrhiza glabra* root at the background.

Chapter IV describes the detail self-assembly studies of *arjunolic acid* and its sodium and potassium salts in different aqueous solvent mixtures and alcohols. Arjunolic acid is a 6-6-6-6-6 pentacyclic trihydroxy triterpenic acid extractable from heavy wood of the medicinal plant *Terminalia arjuna*. Arjunolic acid self-assembled in different aqueous solvent mixtures yielding vesicular structures of nano to micrometer diameters affording thermo-reversible gels. The vesicular self-assemblies have been utilized for the entrapment of different fluorophores including anticancer drug such as doxorubicin. Controlled release of the entrapped drug molecules also has been demonstrated at physiological pH. A dilute ethanolic solution of arjunolic acid (0.5% w/v) formed a strong composite gel with aqueous bark extract (60 mg.L^{-1}) of the

medicinal plant *Terminalia arjuna*. The bark extract of *Terminalia arjuna* is a rich source of antioxidants as well as poly phenols which are well known as an efficient reducing as well as stabilizing agent for the preparation of gold nanoparticles. For this reason, the composite gel of *arjunolic acid* (with the bark extract) was utilized for the preparation of a hybrid gel by *in-situ* generated gold nanoparticles. Anticipating that the alkali metal salts of arjunolic acid will have better solubility in water, we prepared the sodium and potassium salts of arjunolic acid **2** and **3** respectively (Figure 3). Interestingly, both the salts were found to be excellent hydrogelators as well as gelators of a wide range of aliphatic alcohols via vesicular self assemblies. The vesicular self-assemblies of salts were also utilized for the entrapment of different fluorophores including anticancer drug doxorubicin and curcumin.

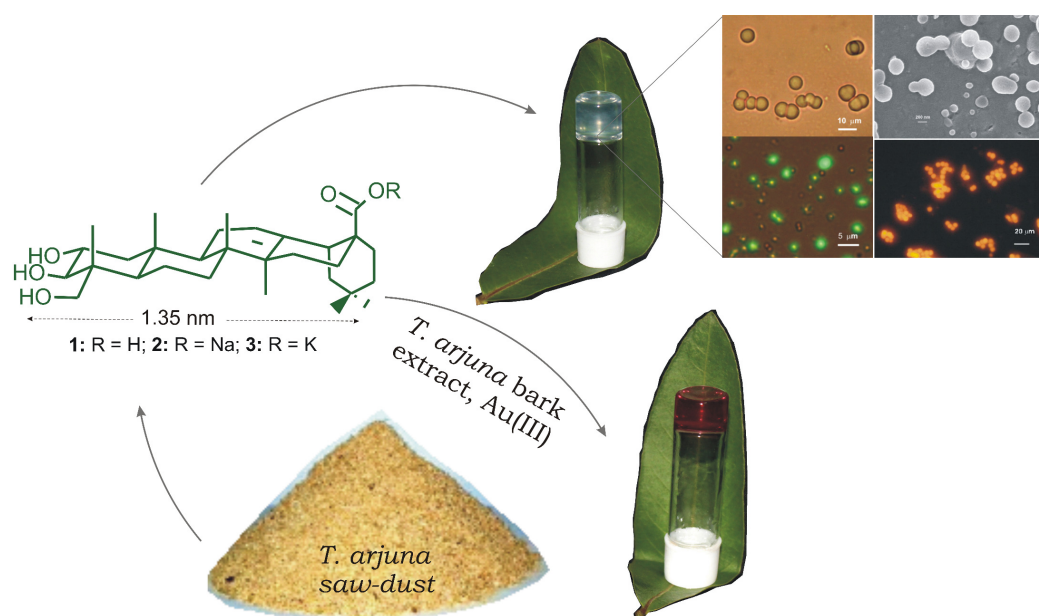
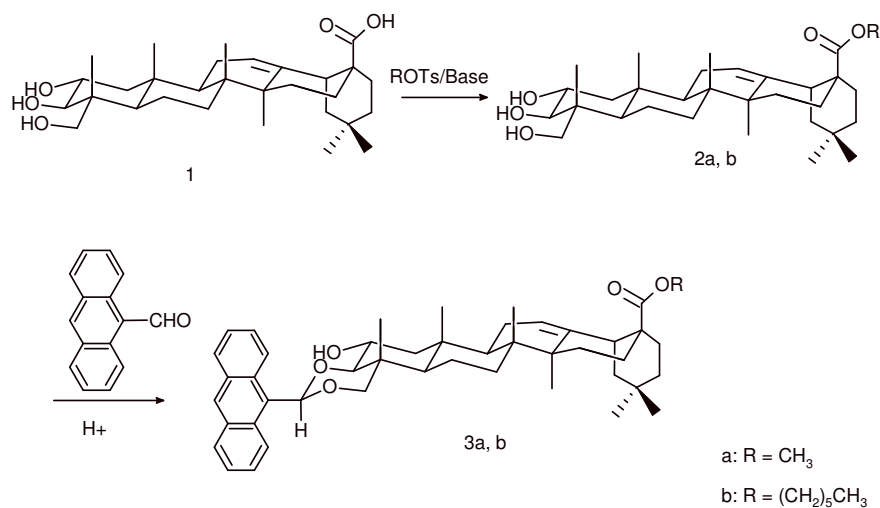
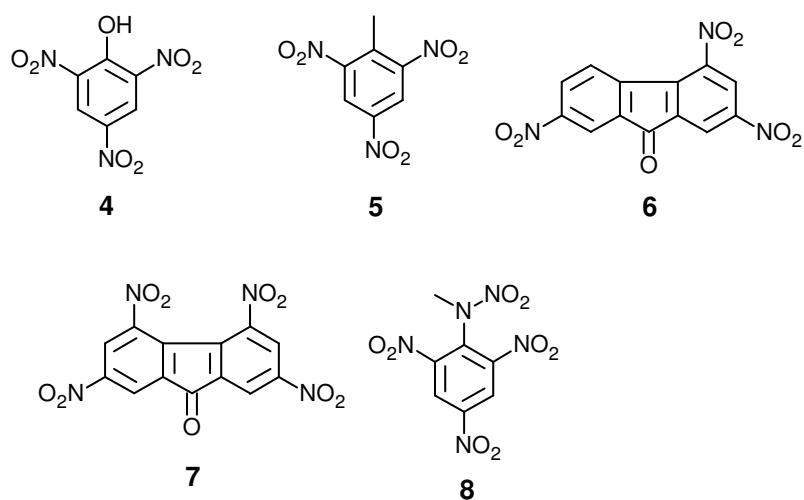


Figure 3: Schematic representation of the formation of gel and gel-gold nanoparticle hybrid material from arjunolic acid **1** extractable from the saw-dust of *Terminalia arjuna* (Inverted vials showing the gels have the leaves of *Terminalia arjuna* in the background).

Chapter V describes the two-component gelation studies of anthrylidene derivatives of alkyl arjunolates with different nitroaromatics. The present study on anthrylidene arjunolate derivatives based charge transfer gels illustrates the versatility of the derivatives as donors with various nitroaromatics as the acceptors in the gelation process. For gelation, the charge transfer interaction is the driving force, which is supported by the appearance of strong CT absorption bands at varied λ_{max} in the visible region depending upon the guest molecules. The intensification of color on going from the sol to the gel phase also supports the crucial role of the CT interaction behind the formation of these gels. Thermodynamic parameters and the free energy change data calculated from the phase-transition diagrams afforded an insight into the stability of the gels. The gelation ability of the anthrylidene derivatives with various nitroaromatics make them very attractive candidates for designing thermochromic switches, sensor devices etc.



Scheme 1: Synthesis of anthrylidene ester derivatives of Arjunolic acid **3a, b**.



Scheme 2: Electron deficient nitroaromatic guests **4-8**.

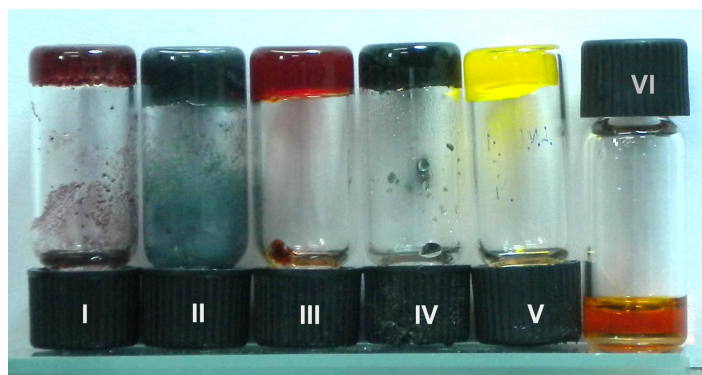


Figure 4: Self-assembly of anthrylidene methyl arjunolate yielding different color gels with different nitroaromatics in organic liquids.