Flower- and Grass-like Self-Assemblies of an Oleanane-Type Triterpenoid Erythrodiol: Application in the Removal of Toxic Dye from Water

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ABSTRACT: Erythrodiol (3β-olean-12-ene-3, 28-diol) \(\text{C}_{30}\text{H}_{50}\text{O}_{2}\) is a nanosized oleanane-type fused 6-6-6-6-6 pentacyclic triterpenoid extractable from the dried leaves of olive (\textit{Olea europia}). One step reduction of oleanolic acid extracted from \textit{Lantana camara} also yields the same compound. The triterpenoid has one secondary \(-\text{OH}\) group attached at C3 of the “A” ring and one primary \(-\text{OH}\) group at C28 present at the junction of the “D” and “E” rings. Here, we report the spontaneous self-assembly of erythrodiol in different neat organic liquids and aqueous-organic liquid mixtures. The nanosized dihydroxy triterpenoid having an oleanane-type lipophilic rigid skeleton self-assembled in liquids, yielding nanosized fibrils, microsized flowers, and grass-like architectures via formation of densely assembled fibrils and petals or 2D sheets. The microstructures of the self-assemblies have been characterized by different techniques like optical microscopy, electron microscopy, atomic force microscopy, FTIR, and wide angle X-ray diffraction studies. The porous self-assemblies having a large surface area obtained from 1 were capable of adsorbing toxic fluorophores like rhodamine-B, rhodamine-6G, methylene blue, and crystal violet (CV). Moreover, removal of the aforementioned toxic pigments has also been demonstrated from their aqueous solutions by using UV−visible spectrophotometry and epifluorescence microscopy.

1. INTRODUCTION

Terpenoids, the largest class of natural products containing a multiple of C5 units, have drawn significant research interests in recent years due to their diversified structural features, interesting self-assembly properties, and the applications of the resulting self-assemblies in advanced functional materials and biological research.1,2 The mono-terpenoids (C10) to higher terpenoids (C15−C40), all having nanometric lengths and properly positioned functional groups, offer innumerable opportunities for their utilization as molecular functional nanos (MFNs).1 The inherently renewable nature of the plant-based terpenoids have drawn significant research interest in recent years for the development of sustainable society. This large and structurally diverse group of natural products of nanometric dimensions and properly positioned functional groups have made them useful as an interesting class of amphiphiles for the study of their self-assembly properties. Though a significant research advancement has taken place on functional metal nanoparticles (FMNPs) and the self-assembly of different class of compounds such as peptides, sugars, steroids, fatty acids, and lipids, only a few examples on the self-assembly of terpenoids have been reported till date.3−16

Previously, we have reported the self-assembly property and applications of several triterpenoids like arjunolic,17,18oleanolic,19 glycyrrhetinic,20 ursolic,21 maslinic,22 corosolic,23 and betulinic acids;24 di-hydroxy lupane-type triterpenoid betulin;25 and C2-symmetric dihydroxy seco-triterpenoid α-onocerin.26 Self-assembly of a macrocyclic diterpenoid crotocembraneic acid has also been demonstrated in aqueous liquids.27 These MFNs spontaneously self-assembled as natural amphiphiles without any functional group transformations. Different morphologies such as vesicles, tubes, flowers, and fibrillar networks were obtained by self-assembly of different terpenoids, indicating structure property relationships though predictability of the morphology of a given terpenoid in a medium is in its infancy.

Erythrodiol 1 is a dihydroxy triterpenoid extractable from olive (\textit{Olea europia}). In plants, erythrodiol is proposed to be

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the precursor of oleanolic acid. It has been shown to possess a wide range of biological activities such as anticancer activity on different cell lines,28–30 antitumor activity, vasorelaxant, and cardio-protective activities.31–33 It is also found to be effective in skin chronic inflammation.34 However, to our knowledge, the self-assembly property of this compound in liquids has not yet been reported.

In this study, we have investigated the self-assembly property of this triterpenoid erythrodiol 1 in different organic liquids and aqueous-organic liquid mixtures. Nanosized fibrils, micro-sized flowers, and grass-like architectures were obtained via formation of densely assembled fibrils and petals or 2D sheets. The morphology of the self-assemblies has been analyzed by SEM, AFM, HRTEM, and wide-angle X-ray diffraction studies. The porous self-assemblies having high surface area were utilized as adsorbents of toxic dyes like crystal violet (CV), methylene blue (MB), rhodamine-B (rho-B), and rhodamine-6G from their aqueous solution, as demonstrated by epifluorescence microscopy as well as UV–vis spectrophotometry.

2. RESULTS AND DISCUSSION

2.1. Isolation of Erythrodiol and Its Structural Characteristics. Oleanolic acid extracted from the root bark of Lantana camara yielded erythrodiol 1 on reduction with LiAlH4 as a white crystalline solid (Scheme 1).7,35 Solvent extraction of the leaves of olive also yielded the same (Scheme 1).36,37 Erythrodiol 1 has a fused 6-6-6-6-6 pentacyclic triterpenoid moiety with two polar “−OH” groups: one attached at the C3 position of the “A” ring and the other −OH is attached at C28 present at the junction of cis-fused “D” and “E” rings. Computations carried out by DFT calculation and by molecular mechanics calculation using Allinger’s MMX algorithm revealed the molecular length of 1.57 nm (Figure S1 and S2). The lipophilic 6-6-6-6-6 fused pentacyclic backbone and the presence of polar functional groups at the two ends of the nanosized triterpenoid backbone makes it a unique amphiphile for studying its self-assembly properties in different liquids (Table 1).

![Scheme 1. Schematic Presentation of Isolation and Synthesis of Erythrodiol 1 and Its Self-Assembly Property Yielding Flowers, Fibers, and Grass-like Architectures](image)

**Table 1. Self-Assembly Studies of Erythrodiol 1**

| entry | medium | conc. (mM) | state |
|-------|--------|-----------|-------|
| 1     | o-xylene | 56.5 | CS |
| 2     | m-xylene | 45.2 | CS |
| 3     | p-xylene | 45.2 | CS |
| 4     | mesitylene | 90.4 | CS |
| 5     | chlorobenzene | 45.2 | CS |
| 6     | o-dichlorobenzene | 56.5 | CS |
| 7     | 2-propanol | 45.2 | CS |
| 8     | EtOH | 22.6 | S |
| 9     | DMSO | 45.2 | S |
| 10    | EtOH-H2O (1:1) | 45.2 | CS |
| 11    | DMSO-H2O (1:1) | 22.6 | CS |
| 12    | H2O | 22.6 | I |

*S = soluble, I = insoluble, CS = colloidal suspension.

(usually 1–5 mg) was dissolved in neat liquids under hot conditions (40–50 °C) with magnetic stirring. For studying the self-assembly in neat liquids, the hot solution was allowed to cool at room temperature and observed visually after 4–8 h. In o-xylene, m-xylene, p-xylene, mesitylene, chlorobenzene, o-dichlorobenzene, and 2-propanol it remained as a colloidal suspension of 1 in the liquids. For study of the self-assembly of 1 in the ethanol–water mixture, the hot solution of 1 in ethanol was mixed with an increasing amount of water till cloudiness appeared, then it was re-dissolved by heating, and then the clear solution was cooled at room temperature. A colloidal suspension of 1 was also obtained in ethanol–water mixture. Similarly, a colloidal suspension was also obtained in DMSO-water.

2.2. Self-Assembly Studies. Compound 1 was only sparingly soluble in most of the common organic liquids and remained insoluble in water. Self-assembly properties of 1 were studied in different types of neat organic liquids and alcohol–water mixture. For this purpose, a weighed amount of 1 from o-xylene by SEM at a higher magnification indicated that the flowers were composed of densely packed petals (2D sheet) with an average thickness of 50–200 nm (Figure 1d,h and Figure S6c,e,f). SEM carried out with the dried self-assemblies of 1 prepared from the colloidal suspensions in m-xylene (2% w/v, 45.2 mM), p-xylene (2% w/v, 45.2 mM), and mesitylene (4% w/v, 90.40 mM) revealed cauliflower-like

![Figure 1. SEM images of dried self-assembled 1 in o-xylene at different concentrations: (a–d) in 2% w/v (45.2 mM), (e–h) in 2.5% w/v (56.50 mM).](image)
flowers having an average diameter of 15–20 μm (Figure 2 and Figures S7 and S8).

![Figure 2](image)

**Figure 2.** Electron microscopy images of dried self-assemblies of 1 (a–c) in m-xylene (2% w/v, 45.2 mM) and (d–f) in mesitylene (4.0% w/v, 90.4 mM).

Though flower-shaped microstructures having a micrometer diameter were obtained from the dried self-assemblies of 1 in four liquids, o-, m-, and p-xlenes, and mesitylene, their shapes and size were not identical. The petals and the arrangement of the petals in the microstructures were also different. This difference might be due to a very fine balance between the polarity of the medium, structure of the solvent molecules, and solvent–solute and solute–solute interactions.

SEM analyses were also carried out with the dried self-assemblies of 1 prepared from chlorobenzene (2% w/v, 45.20 mM) and o-dichlorobenzene (1.5% w/v, 33.90 mM). Investigations of the self-assembled microstructures prepared from dried self-assemblies of 1 in chlorobenzene (2% w/v, 45.20 mM) and o-dichlorobenzene (2% w/v, 45.20 mM) revealed hierarchical self-assembly of molecules yielding a densely packed fibrillar network and grass-like morphology (Figure 3). In chlorobenzene, the fibers were of 22–45 nm in diameter and nano- to micrometer in lengths, whereas the grass leaves observed in o-dichlorobenzene (2% w/v, 45.20 mM) were of several micrometer lengths formed from nanometer diameter fibers (Figure 3 and Figure S9b).

![Figure 3](image)

**Figure 3.** FESEM micrographs of dried self-assemblies of 1: (a) porous nanofibers and (b, c) grass-like architecture in o-dichlorobenzene (2% w/v); (d–f) nano-fibers in chlorobenzene (1.5% w/v).

Flower-like self-assembled nanostructures from inorganic metal oxides and inorganic hybrid nanoparticles such as SnO$_2$, TiO$_2$, ZnO, Fe$_3$O$_4$, and Ni(OH)$_2$ have been reported in the literature, but such flower- and grass-like self-assembled microstructures resembling naturally occurring marigold (*Calendula officinalis*), cauliflower, and grass from nanosized organic molecules are rare.

2.3.2. Transmission Electron Microscopy. To further elucidate the self-assembled microstructures observed by electron microscopy, we carried out HRTEM studies. TEM images obtained from very dilute colloidal suspension of 1 prepared from mesitylene (0.8% w/v, 18.08 mM) in dried conditions clearly indicated micrOSized flowers (Figure 4 and Figure S11).

![Figure 4](image)

**Figure 4.** (a–d) HRTEM image of 1 in mesitylene (1% w/v, 22.6 mM) and (e,f) HRTEM image of 1 in o-xylene (0.8% w/v, 18.08 mM) in a dried state.

**Figure S11c** composed of fibrillar networks and sheets. A TEM micrograph obtained from o-xylene (0.8% v/v, 18.1 mM) also indicated the flower-like objects and gel-like morphology (Figure 4e and Figure S11a,b). Flower-like morphology observed by HRTEM supported the observation by SEM analyses discussed earlier.

2.3.3. AFM Studies. Atomic force microscopy was carried out with the dried self-assemblies of 1 prepared from a dilute colloid of 1 in neat organic liquid such as o- and p-xlenes (0.8% w/v, 18.1 mM), mesitylene (1% w/v, 22.6 mM), and o-dichlorobenzene. Flowers, petals, fibrillar networks, and spherical objects were observed (Figure 5, Figure S12) in the dried self-assemblies prepared from all the liquids supporting our earlier observation from electron microscopy (Figure 1–4).

2.3.4. Optical Microscopy. Optical microscopy (OM) was carried out to investigate the morphology of the self-assemblies of 1 in various neat organic liquids like o-xylene, m-xylene, p-xylene, and mesitylene (2% w/v, 45.20 mM) in their native state. Erythrodiol 1 self-assembled in o-xylene and m-xylene (2% w/v, 45.20 mM) forming microsized spherical objects and flower-like self-assemblies (Figure 6 and Figure S13). Identical images were also observed in p-xylene and mesitylene. The nanosized spherical objects were not observed by OM due to the size limitations in optical microscopy.

2.3.5. FTIR Studies. Self-assembly of the bola-type amphiphile having polar H-bonding groups at the two extreme ends may have been driven by the intermolecular H-bonding along with the dispersive interactions from the large lipophilic rigid terpenoid backbone. To investigate the role of H-bonding in the self-assembly, FTIR spectra were recorded taking the neat powder and the dried self-assemblies prepared from o-, m-, and p-xlenes (2% w/v, 45.2 mM), o-dichlorobenzene (2% w/v, 45.2 mM), and mesitylene (4% w/v, 90.4 mM) and their stretching frequencies were
The presence of identical morphologies at the nanoscale, giving rise to distinct nano- to microsized self-assemblies observed from different liquids.

Figure 5. AFM images of 1 (a,d) in p-xylene (1.0% w/v) and (b,c) in mesitylene (0.8% w/v, 18.08 mM) in a dried state.

Figure 6. OM images of 1 (a) in o-xylene (2% w/v, 45.2 mM) and (b) in mesitylene (2% w/v, 45.2 mM) in a native state.

compared. The –OH stretching frequency of the neat powder of 1 (3354 cm\(^{-1}\)) shifted to 3345, 3346, and 3348 cm\(^{-1}\) in the dried samples prepared from o-, m-, and p-xlenes. The lowering of –OH stretching frequency observed in the dried self-assemblies compared to neat powder indicated stronger intermolecular H-bonding interactions in the self-assemblies (Figure S15) supporting the role of H-bonding during self-assembly.

2.3.6. X-Ray Diffraction Studies. Powder X-ray diffraction studies were carried out to know more detail about the patterns of the self-assemblies. Wide-angle powder XRD studies of neat powder and dried self-assemblies prepared from o-xylene (2.5% w/v, 56.5 mM), m-xylene (2%w/v, 45.2 mM), and p-xylene (2%w/v, 45.2 mM) in the range of 2\(\theta\) = 5–40\(^\circ\) were carried out and their diffraction patterns were compared with neat powder of 1. The wide angle X-ray diffraction peaks observed in the dried self-assemblies of 1 prepared from o- and m-xylene were at \(d = 1.57, 0.78, 0.52\) nm (Table S1), which were in the ratio of 1:1/2:1/3 along with additional peaks. The optimized molecular length of erythrodil 1 being 1.57 nm, a lamellar pattern of self-assembly of the molecules could be considered in the dried and m-xylene. The diffraction pattern of the neat powder also had identical peaks along with additional peaks, though the peaks from the self-assemblies were sharper compared to that in the neat powder indicating comparatively more order assembly of molecules in the self-assemblies (Figure S16 and Table S1). Almost identical \(d\) values (similar type of diffraction patterns) found in all the xerogel samples studied were reflecting the presence of identical morphologies at the nanoscale, giving rise to distinct nano- to microsized self-assemblies observed from different liquids.

2.3.7. Proposed Model for the Self-Assembly of 1. A model for the self-assembly of 1, yielding flowers, grass, and a fibrillar network has been proposed as shown in Figure 7. Erythrodil 1 having a \(\beta\)-amyrin type skeleton can be schematically represented as an unsymmetrical bola-type amphiphile M-spacer-P (Figure 7). It can self-assemble forming a linear 1D chain (Figure 7A,B) via intermolecular H-bonding. The fibrillar network yields the petals and long-leaf like architectures, leading to the formation of flower- and grass-like morphologies, as evident from electron microscopy.

2.4. Adsorption of Fluorophores. Optical and electron microscopies, AFM, and HRTEM analysis of the dried assemblies of 1 prepared from various neat organic liquids confirmed the porous nature of the microsized flower- and grass-like self-assemblies in all the cases. These observations encouraged us to study the adsorption capability of the self-assembled microstructures of 1. Initial adsorption studies of the self-assemblies were carried out with toxic dyes like rhodamine-B (rho-B) and methylene blue (MB). For this study, 1 (2 mg) was dissolved in isopropanol (1% w/v, 200 \(\mu\)L) and was mixed with aqueous rho-B (0.25 mM, 0.03 mL) and cloudiness appeared. Then, the mixture was heated followed by magnetic stirring and allowed to cool at 15 °C for 6 h. Then, an aliquot of 10 \(\mu\)L was taken from the colloidal suspension for studying epifluorescence microscopy. Bright green and red fluorescence observed from the surface of the microsized self-assemblies under fluorescence light indicated that both rhodamine-B and MB were adsorbed on the surface of the porous self-assemblies of 1 (Figure 8a–f and Figure S14).

2.5. Dye Removal Study by UV Spectrophotometry. Toxic dye removal from waste water is of great concern for environmental reasons during the last few decades. Adsorption of fluorophores in the self-assemblies as observed by epifluorescence microscopy inspired us to investigate whether the porous self-assemblies of the flower and fibrillar network could be capable of removing the toxic dyes like rhodamine-B, methylene blue (MB), crystal violet (CV), and...
rhodamine-6G from their respective aqueous solution. For these studies, aqueous solutions of dyes were prepared by dissolving a weighed amount of dye in distilled water. For the preparation of aqueous solution of cationic dye of CV, a weighed amount (4 mg) of CV was taken in a clean dried vial and dissolved in 2 mL distilled water and from this solution, 10 μL was taken and was further diluted to 2 mL by adding distilled water to prepare aqueous CV solution (10 mg/L). By following the similar procedure, aqueous solutions of rho-B, MB, and rhodamine-6G were prepared having the concentration of 10 mg/L. Colloidal self-assemblies of 1 were prepared by dissolving 5 mg of 1 in 0.5 mL dry distilled o-dichlorobenzene (22.50 mM) in four clean vials. Then, 2 mL aqueous solution of all the dyes prepared were placed carefully on the organic colloidal suspension of 1 (22.50 mM) and absorbance were measured taking the aqueous aliquot of 2 mL from the upper layer very carefully at different time intervals with UV–visible spectrophotometry. It was evident from the results of UV–visible spectrophotometry that with increasing time, absorbance was decreased for all the cationic dye solutions. For MB and CV, absorbance decreased within 45 min–1 h and for rhodamine-B and rhodamine-6G, absorbance decreased within 1–1.5 h. Control partition experiments carried out with all the above dyes did not show significant removal even after 4–6 h (Figure S17). All these observations support the absorbing efficiency of the porous self-assembled microstructures (Figure 9). These investigations also lead the way for the removal of toxic carcinogenic dyes from water paving the way for sustainable removal of dyes from contaminated water based upon renewable terpenoids.

3. CONCLUSIONS

In conclusion, spontaneous formation of flower- and grass-like porous self-assemblies of oleanane-type triterpenoid erythrodiol has been reported. According to our knowledge, this is the first report of the formation of flower- and grass-like microstructures by naturally occurring 6-6-6-6-6 fused pentacyclic dihydroxy oleanane-type triterpenoid. Detailed morphological characterization of the self-assemblies has been carried out by AFM, optical microscopy, SEM, FESEM, HRTEM, and wide-angle X-ray diffraction studies. Utilization of the porous self-assemblies has been demonstrated for the removal of toxic dyes such as rho-B, CV, and MB from their aqueous solution. The studies described here demonstrate the generation of advanced materials based on natural terpenoids for applications in material science and medicine.
4. EXPERIMENTAL SECTION

4.1. Dye Removal Study. The colloidal self-assemblies of 1 prepared from o-dichlorobenzene were used for the study of its dye removal ability. Compound 1 (5 mg) was taken in a vial and dissolved in distilled o-dichlorobenzene (0.5 mL) under hot conditions, and the resulting solution was allowed to cool at 15 °C temperature for 6 h. For the preparation of aqueous solution of cationic dye CV, a weighed amount (4 mg) of CV solutions. Colloidal self-assemblies of CV solution (10 mg/L, 0.02 mM). By following the similar procedure, aqueous solution of rho-B (0.02 mM), MB (0.03 mM), and rhodamine-6G (0.02 mM) were prepared having the concentration of 10 mg/L for all the prepared aqueous solutions. Colloidal self-assemblies of 1 were prepared by dissolving 5 mg of 1 in 500 μL distilled o-dichlorobenzene (22.50 mM) in four clean vials. Then, 2 mL aqueous solution of all the dyes prepared were placed carefully on the organic colloidal suspension of 1 (22.50 mM) and absorbance were measured taking the aqueous aliquot of 2 mL from the upper layer very carefully in a quartz cuvette (2 mm path length), and the absorption was measured at \( \lambda_{\text{max}} = 586 \text{ nm} \) (CV), \( \lambda_{\text{max}} = 660 \text{ nm MB} \), \( \lambda_{\text{max}} = 550 \text{ nm} \) (rho-B), and \( \lambda_{\text{max}} = 27 \text{ nm} \) (rho-6G) after different time intervals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c04291.

General information regarding self-assembly studies, isolation, method of sample preparation, optical microscopy, electron microscopy, HRTEM, AFM, XRD, FTIR, and NMR (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Bag, B. G.; Barai, A. C.; Hasan, S. N.; Panja, S. K.; Ghorai, S.; Patra, S. Terpenoids, nano-entities and molecular self-assembly. Pure Appl. Chem. 2020, 567–577.

(2) Whitesides, G. M.; Grzybowski, B. Self-Assembly at All Scales. Science 2002, 295, 2418–2421.

(3) Carretti, E.; Bonini, M.; Dei, L.; Berrie, B. H.; Angelova, L. V.; Baglioni, P.; Weiss, R. G. New Frontiers in Materials Science for Art Conservation: Responsive Gels and Beyond. Acc. Chem. Res. 2010, 43, 751–760.

(4) Weiss, R. G.; Terech, P. Molecular Gels. In Materials with Self-Assembled Fibrous Networks; Springer: Dordrecht, (2006).

(5) Dong, R.; Zhou, Y.; Zhu, X. Supramolecular Dendritic Polymers: From Synthesis to Applications. Acc. Chem. Res. 2014, 47, 2006–2016.

(6) Datta, S.; Bhattacharya, S. Multifarious facets of sugar-derived molecular gels: molecular features, mechanisms of self-assembly and emerging applications. Chem. Soc. Rev. 2015, 44, 5596–5637.

(7) Bag, B. G.; Majumdar, R. Self-assembly of Renewable Nano-sized Triterpenoids. Chem. Rec. 2017, 17, 841–873.

(8) Perham, R. N. Self-Assembly of Biological Macromolecules. Phil. Trans. R. Soc. Lond. B. 1975, 272, 123–136.

(9) Okesola, B. O.; Smith, D. K. Applying low-molecular weight supramolecular gelators in an environmental setting — self-assembled gels as smart materials for pollutant removal. Chem. Soc. Rev. 2016, 45, 4226–4251.

(10) Ozin, G. A.; Hou, K.; Lotsch, B. V.; Cademartiri, L.; Puzzo, D. P.; Scottonella, F.; Ghadimi, A.; Thomson, J. Nanofabrication by self-assembly. Mater. today. 2009, 12, 12–23.

(11) Bhattacharya, S.; Samanta, S. K. Soft-Nanocomposites of Nanoparticles and Nanocarbons with Supramolecular and Polymer Gels and Their Applications. Chem. Rev. 2016, 116, 11967–12028.

(12) Seeman, N. C. Nanomaterials Based on DNA. Annu. Rev. Biochem. 2010, 79, 65–87.

(13) Vemula, P. K.; John, G. Crops: A Green Approach toward Self-Assembled Soft Materials. Acc. Chem. Res. 2008, 41, 769–782.

(14) Fuhrop, J. H.; Schneider, P.; Boekema, E.; Helfrich, W. Lipid Bilayer Fibers from Diasteroeromic and Enantiomeric N-Octyldadronamines. J. Am. Chem. Soc. 1988, 110, 2861–2867.

(15) Grzelczak, M.; Vermunt, J.; Furst, E. M.; Láz-Márzán, L. M. Directed Self-Assembly of Nanoparticles. ACS Nano 2010, 4, 3591–3605.

(16) Ulbrich, K.; Holá, K.; Šuh, V.; Bakandritsos, A.; Tuček, J.; Zboňil, R. Targeted Drug Delivery with Polymers and Magnetic Nanoparticles: Covalent and Noncovalent Approaches, Release Control, and Clinical Studies. Chem. Rev. 2016, 116, 5338–5431.

(17) Bag, B. G.; Majumdar, R. Vesicular self-assembly of a natural triterpenoid arjunolic acid in aqueous medium: study of entrapment properties and in situ generation of gel–gold nanoparticle hybrid material. RSC Adv. 2014, 4, 53327–53334.

(18) Bag, B. G.; Maiti, G. C.; Dinda, S. K. Donor–Acceptor Interaction Promoted Gelation: Visual Observation of Color Change. Org. Lett. 2006, 8, 5457–5460.

(19) Bag, B. G.; Paul, K. Vesicular and Fibrillar Gels by Self-Assembly of Nanosized Oleanolic Acid. Asian J. Chem. 2012, 1, 150–154.

(20) Bag, B. G.; Majumdar, R. Self-assembly of a renewable nano-sized triterpenoid 18β-glycyrrhetinic acid. RSC Adv. 2012, 2, 8623–8626.

(21) Bag, B. G.; Das, S.; Hasan, S. N.; Barai, A. C. Nanoarchitectures by hierarchical self-assembly of ursolic acid: entrapment and release of fluorophores including anticancer drug doxorubicin. RSC Adv. 2017, 7, 18136–18143.

(22) Bag, B. G.; Hasan, S. N.; Ghorai, S.; Panja, S. K. First self-assembly of a dihydroxy triterpenoid maslinic acid yielding vesicles. ACS Omega 2019, 4, 7684–7690.

(23) Bag, B. G.; Garai, C.; Ghorai, S. Vesicular self-assembly of a natural ursane-type dihydroxy-triterpenoid corosolic acid. RSC Adv. 2019, 9, 15190–15195.

(24) Bag, B. G.; Dash, S. S. First self-assembly study of betulinic acid, a renewable nano-sized, 6-6-6-6-5 pentacyclic monohydroxy triterpenic acid. Nanoscale 2011, 3, 4564–4566.
(25) Bag, B. G.; Dash, S. S. Hierarchical Self-Assembly of a Renewable Nanosized Pentacyclic Dihydroxy-triterpenoid Betulin Yielding Flower-Like Architectures. *Langmuir* 2015, 31, 13664–13672.

(26) Bag, B. G.; Hasan, S. N.; Pongsamorn, P.; Thasana, N. First Hierarchical Self-Assembly of a Seco-Triterpenoid α-Onocerin Yielding Supramolecular Architectures. *ChemistrySelect* 2017, 2, 6650–6657.

(27) Bag, B. G.; Barai, A. C.; Wijesekera, K.; Kittaakoop, P. First Vesicular Self-Assembly of Crotocembraneic Acid, a Nano-Sized Fourteen Membered Macrocyclic Diterpenic Acid. *ChemistrySelect* 2017, 2, 4969–4973.

(28) Juan, M. E.; Wenzel, U.; Daniel, H.; Planas, J. M. Erthrodial, a natural triterpenoid from olives, has antiproliferative and apoptotic activity in HT-29 human adenocarcinoma cells. *Mol. Nutr. Food Res.* 2008, 52, 595–599.

(29) Allouche, Y.; Warleta, F.; Campos, M.; Sánchez-Quesada, C.; Uceda, M.; Beltrán, G.; Gaforio, J. J. Antioxidant, antiproliferative, and pro-apoptotic capacities of pentacyclic triterpenes found in the skin of olives on MCF-7 human breast cancer cells and their effects on DNA damage. *J. Agric. Food Chem.* 2011, 59, 121–130.

(30) Gedara, S. R.; Galala, A. A. New cytotoxic spirostane saponin and biflavonoid glycoside from the leaves of *Acacia saligna* (Labill.) H.L. Wendl. *Nat. Prod. Res.* 2014, 28, 324–329.

(31) Rodríguez, R. R.; Herrera, M. D.; Perona, J. S.; Gutierrez, V. R. Potential vasorelaxant effects of oleanolic acid and erythrodial, two triterpenoids contained in ‘orujo’ olive oil, on rat aorta. *J. Geophys. Res. Oceans* 2004, 92, 635–642.

(32) Allouche, Y.; Beltrán, G.; Gaforio, J. J.; Uceda, M.; Mesa, M. D. Antioxidant and antiherapeutic activities of pentacyclic triterpenic diols and acids. *Food Chem. Toxicol.* 2010, 48, 2885–2890.

(33) Martín, R.; Miana, M.; López, R. J.; Martínez, E. M.; Gómez-Hurtado, N.; Delgado, C.; Bartolomé, M. V.; Román, J. A. S.; Cordova, C.; Lahera, V.; Nieto, M. L.; Cachoibeiro, V. DIOL triterpenes block proliferative effects of angiotensin II and protect from cardiac hypertrophy. *PLoS One* 2012, 7, e41545.

(34) Maínez, S.; Recio, M. C.; Giner, R. M.; Rios, J.-L. Effect of selected triterpenoids on chronic dermal inflammation. *Eur. J. Pharmacol.* 1997, 334, 103–105.

(35) Wu, B. Y. T.; Parks, L. M. Reduction of Triterpene Acids with Lithium Aluminohydride. *J. Am. Pharm. Assoc.* 1950, 39, 475–476.

(36) Altwu, A.; Ok, S. NMR Analysis and Diffusion Coefficient Determination of Minor Constituents of Olive Oil: Combined Experimental and Theoretical Studies. *J. Chem. Eng. Data* 2012, 57, 2619–2624.

(37) Sánchez-Quesada, C.; Lopez-Biedma, A.; Warleta, F.; Campos, M.; Beltrán, G.; Gaforio, J. J. Bioactive Properties of the Main Triterpenes Found in Olives, Virgin Olive Oil, and Leaves of *Olea europaea*. *J. Agric. Food Chem.* 2013, 61, 12173–12182.

(38) Zhao, Y. F.; Sun, Y. P.; Yin, X.; Yin, G. C.; Wang, X. M.; Jia, F. C.; Liu, B. Effect of Surfactants on the Microstructures of Hierarchical SnO2 Blooming Nanoflowers and their Gas-Sensing Properties. *Nanoscale Res. Lett.* 2018, 13, 250.

(39) Jo, W.-K.; Natarajan, T. S. *ACS Appl. Mater. Interfaces* 2015, 7, 17138–17154.

(40) Sun, Y.; Wang, L.; Yu, X.; Chen, K. Facile synthesis of flower-like 3D ZnO superstructures via solution route. *CrystEngComm* 2012, 14, 3199–3204.

(41) Zhong, L. S.; Hu, J. S.; Liang, H. P.; Cao, A. M.; Song, W. G.; Wan, L. J. Self-Assembled 3D Flowerlike Iron Oxide Nanostructures and Their Application in Water Treatment. *Adv. Mater.* 2006, 18, 2426–2431.

(42) Parveen, N.; Cho, M. H. Self-Assembled 3D Flower-Like Nickel Hydroxide Nanostructures and Their Supercapacitor Applications. *Sci. Rep.* 2016, 6, 1–10.

(43) Bhosale, R. S.; al Kobaisi, M.; Bhosale, S. V.; Bhargava, S.; Bhosale, S. V. Flower-like supramolecular selfassembly of phosphoric acid appended naphthalene diimide and melanine. *Sci. Rep.* 2015, DOI: 10.1038/srep14609.