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Review

# Harnessing Glycolipids for Supramolecular Gelation: A Contemporary Review

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Cite This: *ACS Omega* 2024, 9, 25513−25538

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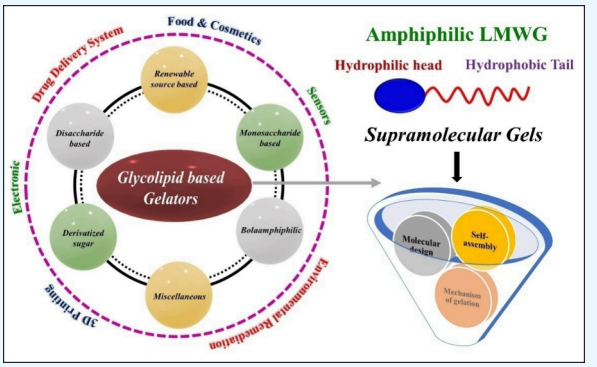
**ABSTRACT:** Within the scope of this review, our exploration spans diverse facets of amphiphilic glycolipid-based low-molecular-weight gelators (LMWGs). This journey explores glycolipid synthesis, self-assembly, and gelation with tailorable properties. It begins by examining the design of glycolipids and their influence on gel formation. Following this, a brief exploration of several gel characterization techniques adds another layer to the understanding of these materials. The final section is dedicated to unraveling the various applications of these glycolipid-based supramolecular gels. A meticulous analysis of available glycolipid gelators and their correlations with desired properties for distinct applications is a pivotal aspect of their investigation. As of the present moment, there exists a notable absence of a review dedicated exclusively to glycolipid gelators. This study aims to bridge this critical gap by presenting an overview that provides novel insights into their unique properties and versatile applications. This holistic examination seeks to contribute to a deeper understanding of molecular design, structural characteristics, and functional applications of glycolipid gelators by offering insights that can propel advancements in these converging scientific disciplines. Overall, this review highlights the diverse classifications of glycolipid-derived gelators and particularly emphasizes their capacity to form gels.




## 1. INTRODUCTION

Supramolecular chemistry has gained an ever-growing significance in multiple areas of research.[1] Jean-Marie Lehn has described supramolecular chemistry as "the chemistry of molecular assemblies and the intermolecular bond" and more comprehensively defined it as "chemistry beyond the molecule."[2] The self-assembly phenomenon is an offshoot in supramolecular chemistry that has grown into a developed field in interdisciplinary research. When gelator molecules self-assemble, the resultant supramolecular network can immobilize the solvent molecules to form a gel. Developing supramolecular gels with specified properties, biocompatibility, and responsiveness to stimuli poses a significant challenge.[3,4] Supramolecular chemists aim to replicate the intricate processes employed by nature in building biological structures and functional biosystems vital for sustaining life.

A gel is defined as a semisolid-like material containing both solid and liquid constituents with the solid component forming a mesh or network of aggregates that immobilizes the liquid component. The term "gel" was coined by Scottish chemist Thomas Graham in the 19th century by clipping from gelatin. A gel is semisolid with qualities that can range from soft and weak to rigid and durable. Gels result from a combination of gelators (solid phase) within the solvent (liquid phase) where the gelator molecules can form a 3D mesh network. On the basis of some basic parameters, gels can be classified into different categories, which is demonstrated in Figure 1. Generally, there are two main types of gelators, i.e., polymers and small molecules. Molecular gels formed by small organic compounds are termed as low-molecular-weight gelators (LMWGs).[5−7] Formation of a 3D gel network by LMWG includes noncovalent interactions, such as electrostatic interactions, van der Waals interactions, hydrogen bonding, $\pi-\pi$ stacking, etc., and the resultant gel is known as a "supramolecular gel."[8] LMWGs have a molecular mass less than 3000 Da. Depending upon the polarity of the solvent used, LMWGs can be further classified into two classes: (a) low-molecular-weight organogelators (LMOGs), which entrap organic solvents, and (b) low-molecular-weight hydrogelators (LMHGs), which entrap water. If the gels consist of oil as the solvent phase, they can be referred to as oleogels. Because of variations in the solvent properties, these oleogels can be easily distinguished from organogels.

In 1974, Paul Flory recognized four categories of gels: (a) high-order lamellar gels (e.g., phospholipids), (2) disordered

Received: January 30, 2024
Revised: April 12, 2024
Accepted: May 17, 2024
Published: June 6, 2024

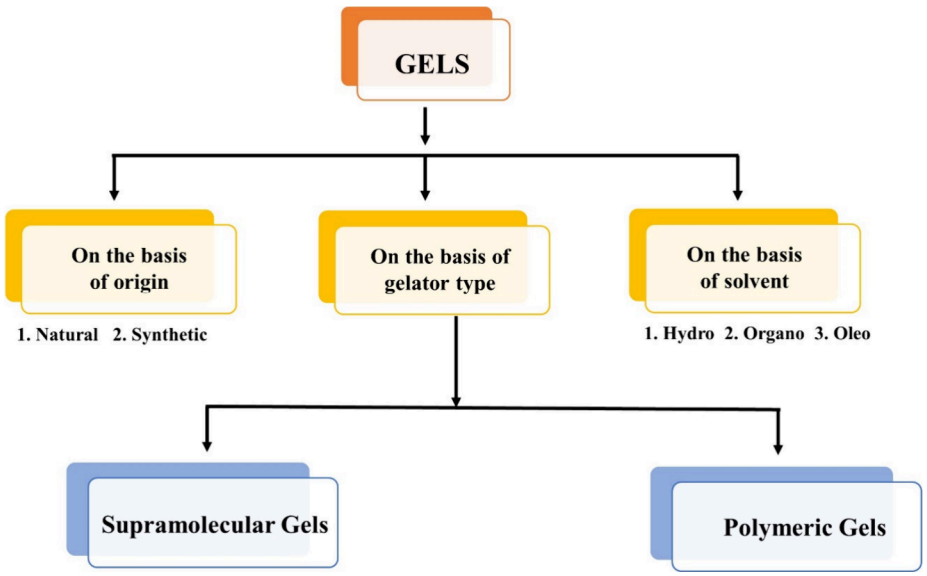



**Figure 1.** Classification of gels.

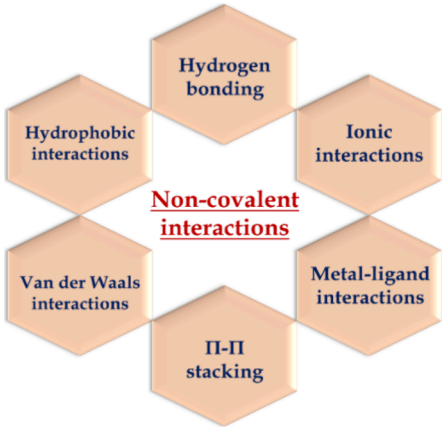



**Figure 2.** Noncovalent interactions involved in the formation of a supramolecular gel network.

covalent networks (e.g., vulcanized rubber), (3) semiordered physical networks (e.g., gelatin), and (4) disordered particulate gels (e.g., reticular fiber networks).[9] Supramolecular gels can be categorized into the fourth category according to Flory and consist of LMWGs self-assembled into a network structure. Supramolecular gels build their framework by noncovalent interactions (Figure 2) and self-assemble to form hierarchical structures. Such soft materials offer exciting novel applications. The hierarchical architecture of molecular gels can be modulated by making suitable choices of solvents and LMWGs.[10−12] They can be used as the template for the synthesis of nanoparticles,[13] in the designing of inorganic material,[14] as therapeutic agents,[15] in photodynamic therapy,[16] drug encapsulation and release,[17] etc. Supramolecular hydrogels possess biocompatibility and biodegradability and can produce good alternatives for polymeric hydrogels. Polymeric gelators mainly include macromolecular compounds that are capable of

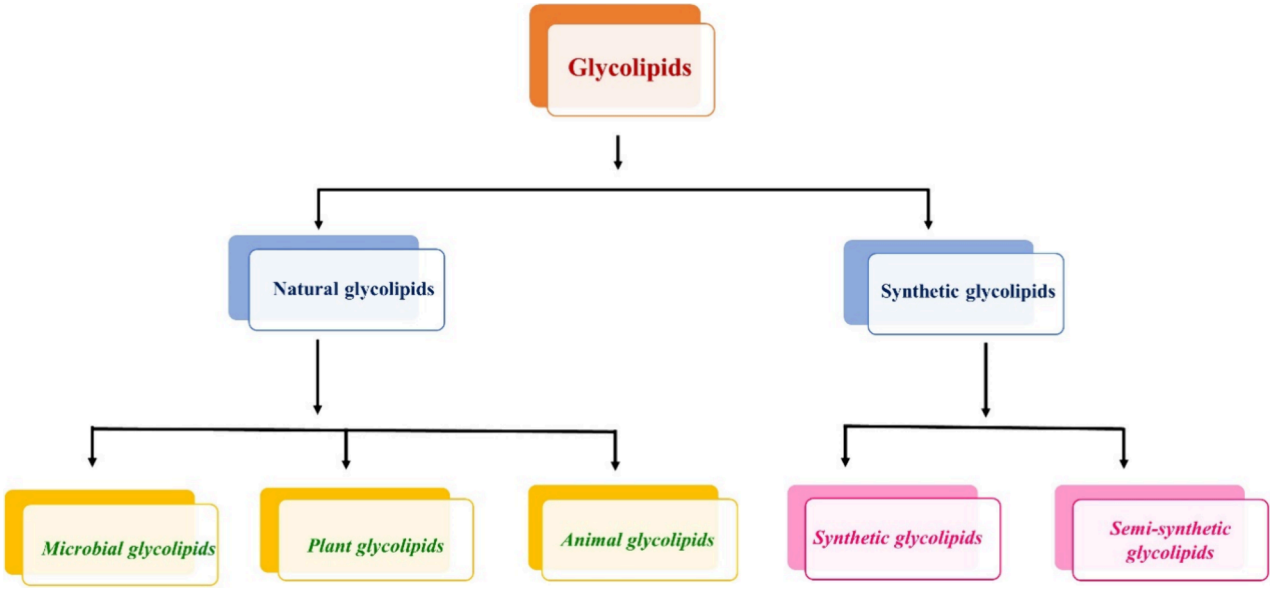



**Figure 3.** Classification of the glycolipids.



https://doi.org/10.1021/acsomega.4c00958
ACS Omega 2024, 9, 25513−25538

inducing gel formation.[18] Such gelators usually establish their gel networks through either noncovalent or covalent forces with a wide range of applications.[19,20]

Over the past few decades, there has been a growing fascination among researchers with reports on LMWGs and their associated gel formations. Numerous reviews have been disseminated, shedding light on various facets of supramolecular gels in literature.[21−25] The exploration and study of diverse types of LMWGs have been undertaken, driven by the intriguing implications of supramolecular chemistry for both material science and biochemistry. The substantial volume of literature dedicated to the subject of supramolecular gels and their chemistry highlights the considerable potential these materials hold within the realm of soft materials, presenting a broad spectrum of applications.

## 2. GLYCOLIPIDS AND THEIR CLASSIFICATION

Glycolipids, a lipid subclass characterized by the presence of a covalently linked carbohydrate moiety to the hydrophobic part, such as fatty acids. Glycolipids are amphiphilic molecules that consist of both hydrophobic and hydrophilic parts.[26,27] The classification of glycolipids on the basis of their origin is a well-established approach. On the basis of their source of origin, glycolipids can be classified into the following categories (Figure 3):

(a) **Natural glycolipids**: These glycolipids are derived from nature. They can be further classified into the following classes.[28]
   (i) *Microbial glycolipids*: These include rhamnolipids, sophorolipids, trehalolipids, and mannosylerythritol lipids.
   (ii) *Plant glycolipids*: These include galactolipids, sulfolipids, and saponins.
   (iii) *Animal glycolipids*: These include glycoglycerolipids, glycosphingolipids, and glycosylphosphatidylinositol.

(b) **Synthetic glycolipids**: These synthetic glycolipid molecules are synthesized in laboratories. They can be further classified into the following classes.
   (i) *Synthetic glycolipids*: These are entirely created/synthesized in the laboratory.[26]
   (ii) *Semisynthetic glycolipids:* These are derived from naturally occurring substances and then modified in the laboratory.[29]

## 3. MECHANISMS OF GELATION

The process of gelation involves the immobilization of a significant volume of solvent by a minimum concentration of gelators, which underscores its inherent complexity. It is commonly understood that gelator molecules organize into an extensive 3D network, thereby entrapping solvent molecules through different mechanisms and providing a gel-like material. In the context of supramolecular gels, this network is characterized by a variety of noncovalent interactions, including hydrogen bonding, $\pi-\pi$ stacking, hydrophobic interactions, charge transfer, donor−acceptor interactions, and metal−ligand coordination.[30−34] This 3D network is referred to as a self-assembled fibrillar network (SAFiN) generated through the intertwining of fibers arising from the self-assembly of gelator molecules.[35,36] It is worth noting that in certain cases the components of SAFiN may not always exhibit a fibrillar nature.[6] In the current landscape, there has been increased attention toward LMWGs because of their spontaneous formation of diverse self-assembled 3D nanostructures. These structures include helices, fibers, ribbons, sheets, particles, rods, tapes, strands, rings, tubules, globules, micelles, and vesicles.[22]

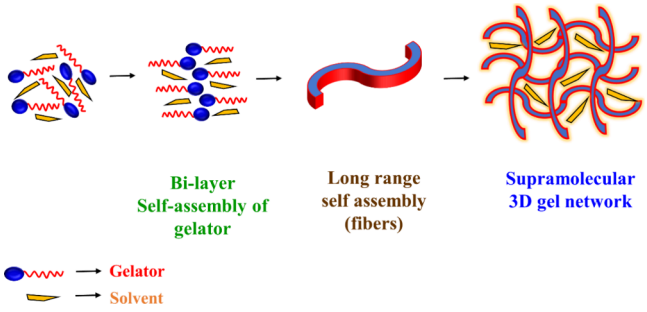



**Figure 4.** Schematic representation demonstrating the mechanism involved in the formation of the supramolecular 3D fibrillar gel network.

To understand the mechanism leading to gel formation, a gel can be fragmented into primary, secondary, and tertiary structures. The primary structure is governed by molecular-level recognition events fostering anisotropic 1D/2D aggregation of gelator molecules (angstrom to nanometer scale). At the secondary level, different morphologies of aggregates are defined by the molecular structure (nanometer to micrometer scale). Various morphologies are observed, including micelles, vesicles, lamellae, and amorphous or crystalline precipitates formed in several modes. Lastly, the tertiary structure of a gel entails the interaction among individual aggregates, thereby ultimately deciding gel formation (micro- to millimeter scale).[37] Overall, the gelation mechanism of supramolecular gelators depends on some important features, such as (a) formation of 1D/2D aggregates via gelator solvent interactions, (b) interweaving of these aggregates to form a 3D network, and (c) proper balance between precipitation and solubilization of gelator.[21,38] One of the representative mechanisms involving the formation of a 3D fibrillar network can be perceived in Figure 4. Hence, the design of new gelator moieties via incorporation of some specific features is an important task. In supramolecular gels, many parameters can be adjusted to tune their properties as per desired applications.[39,40]

It is widely accepted that nanofiber networks, which form the fundamental structure of supramolecular materials, arise from molecular self-assembly. Diverging from the conventional self-assembly mechanism, several other types of gelation mechanisms are explored in the literature. On the basis of the mechanism, the gel morphology will be decided. In another instance, a noncrystallographic branching mechanism was identified by Liu et al. for the formation of fractal fibrous structures in supramolecular gel networks. In this case, the growth of nanofibers in fractal networks occurs through a process of crystallization. In instances of fractal growth, the formation of growing fractal aggregates rather than uniform crystals is observed.[41−43] Also, the basic mechanisms of crystal nucleation and growth are majorly involved in the formation of multilevel crystals. In some studies, it has been demonstrated that gelation in small molecule gels follows a crystallization-controlled process that involves the nucleation and growth of crystallite components, specifically fibers.[44] In another gelation mechanism, a transition from a coagel state to a gel phase is observed when dispersions of a vitamin C-derived surfactant are heated. This interesting transition is attributed to the collapse of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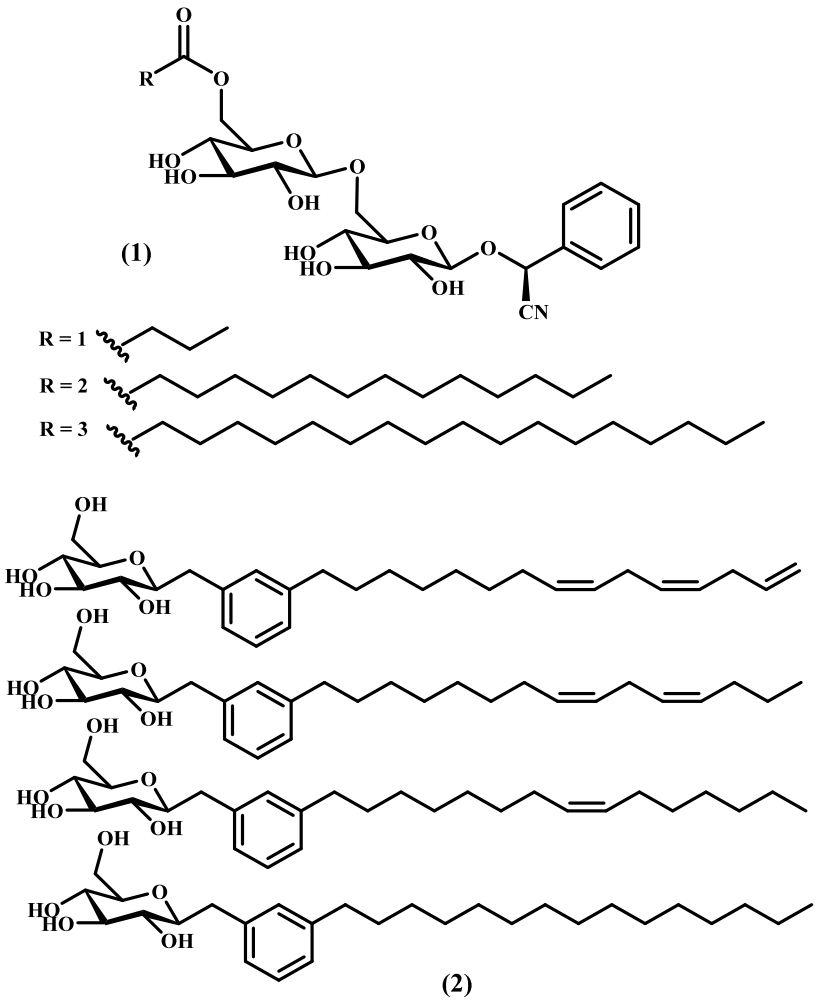


**Figure 5.** Structures representing glycolipid gelators based on renewable sources.

the tightly packed lamellar phase, which loses hydration upon heating. It includes the formation of the gel state upon heating and is characterized by an anisotropic expansion of the lamellar structure. In this process, a 3D network of interconnected lamellar structures is constructed through the aggregation of fibrillar crystals.[45] George and co-workers studied a new isodesmic process in which a coronene bisimide derivative aggregated into 1D fibers.[46] Reports of this kind are genuinely captivating and beneficial for expanding our knowledge.

As lipids possess the ability to self-assemble into diverse soft structures,[47,48] there is a further possibility of either isotropic formations characterized by entangled fibers or anisotropic structures, such as lamellar arrangements. In contrast to conventional isotropic hydrogels featuring a fibrillar network, attention has recently shifted to a subset of anisotropic hydrogels with a distinct 1D periodic lamellar structure.[49−51] Baccile and co-workers reported a novel category of lipid lamellar hydrogels comprising a single bolaform glycosylated lipid. These lipids self-organize into flat interdigitated membranes, supported by electrostatic repulsion, and form stacked lamellar domains on a micrometer scale.[52,53] It has been also observed that the same molecule can exhibit various phases, including micellar, vesicular, fibrillar, and wormlike structures, through pH modulation or the selection of suitable metal ions.[54,55]

In another mechanism, the rational molecular design of amphiphiles on the basis of the self-assembly into helically based nanotubes is thoroughly discussed.[56] In such a process, assembly of asymmetric amphiphilic monomers produced nanotube hydrogels, which encapsulated chemically denatured proteins in nanotube channels and also assisted in transforming the proteins into their refolded states.[57] Transition of amphiphilic molecules to form nanotubes and three types of microtubes is reported by Masuda et al., and the inner diameters of unsymmetrical monolayer lipid membrane nanotubes were controlled by varying the spacer chain length.[58] Similarly, vesicles and vesicle gels represent a class of self-organizing structures, followed by their respective mechanisms. These structures vary in size, spanning from ultrasmall unilamellar vesicles (USUV) with radii of 4−10 nm to large unilamellar vesicles (LUV) and multilamellar vesicles (MLV) exceeding 20 $\mu$m in diameter.[59] In the literature, a metal-coordinated supramolecular gelator complex assembles into vesicles, then fibers, and then lamellae; the process responding to concentration, temperature, and chloride ions is reported.[60]

The mechanism of supramolecular gelation is complex and can vary depending on the many factors involved. As is widely known, the assembled morphology of amphiphiles is mainly determined by their molecular structures. Small alterations in the molecular structure of amphiphiles offer a means of adjusting their morphology. However, it is important to ensure that these modifications do not compromise the intended structure. In self-assembly structures produced by chiral molecular packing,


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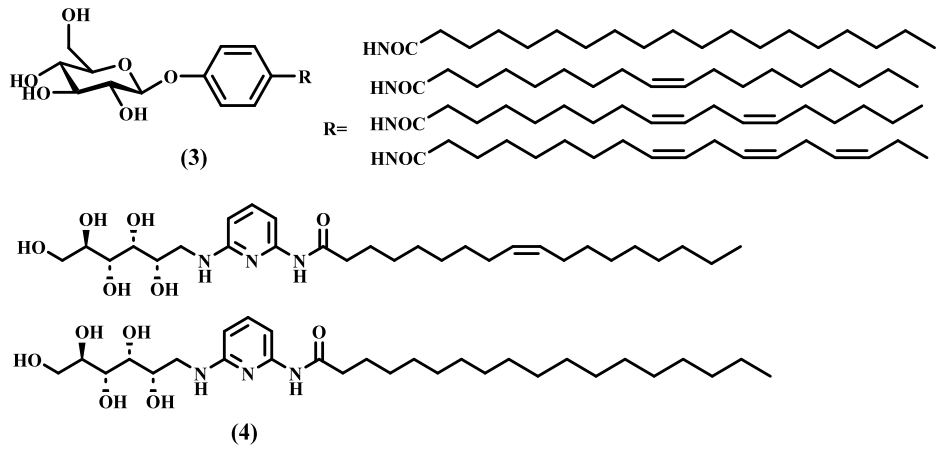


**Figure 6.** Structures representing glycolipid gelators based on renewable sources.

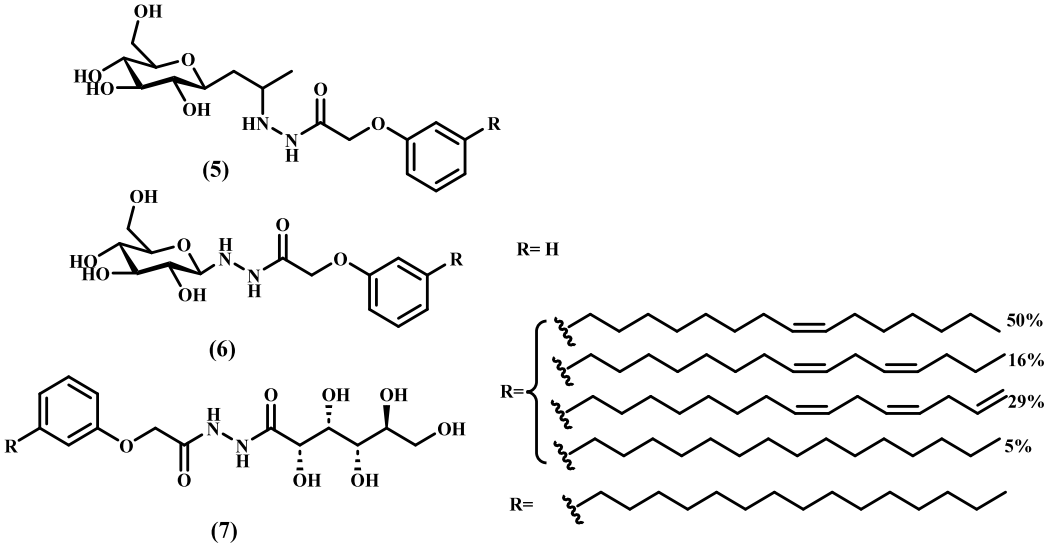


**Figure 7.** Structures representing glycolipid gelators based on renewable sources.

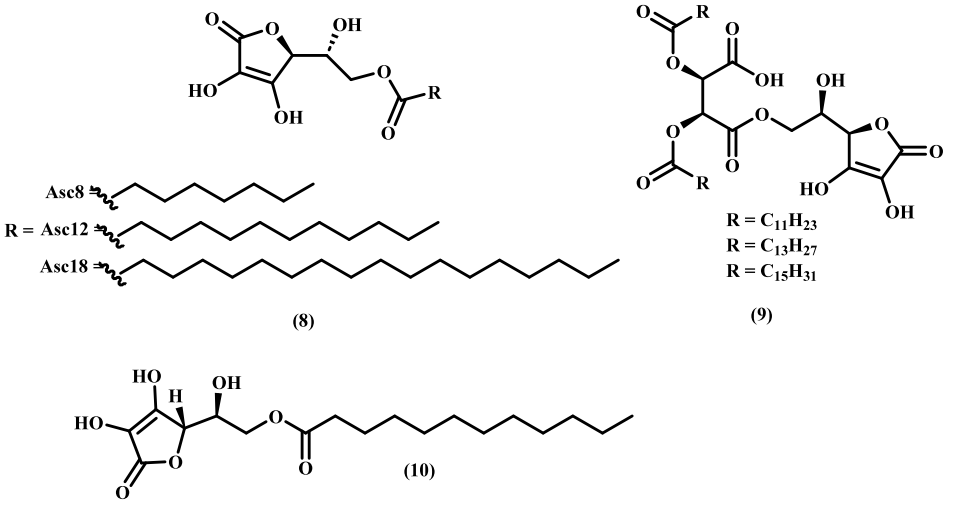


**Figure 8.** Structures representing glycolipid gelators based on renewable sources.

modifications to the headgroup and interfacial region play a pivotal role.[38] Varying hydrophobic chain lengths and headgroup structures influence the molecular packing of amphiphiles in their self-assembled structures.[17,48] However, the position and amount of unsaturation in the hydrophobic tails can also affect the morphology.[61] The type and nature of the solvents are responsible for deciding the morphology of the aggregates too.[62]



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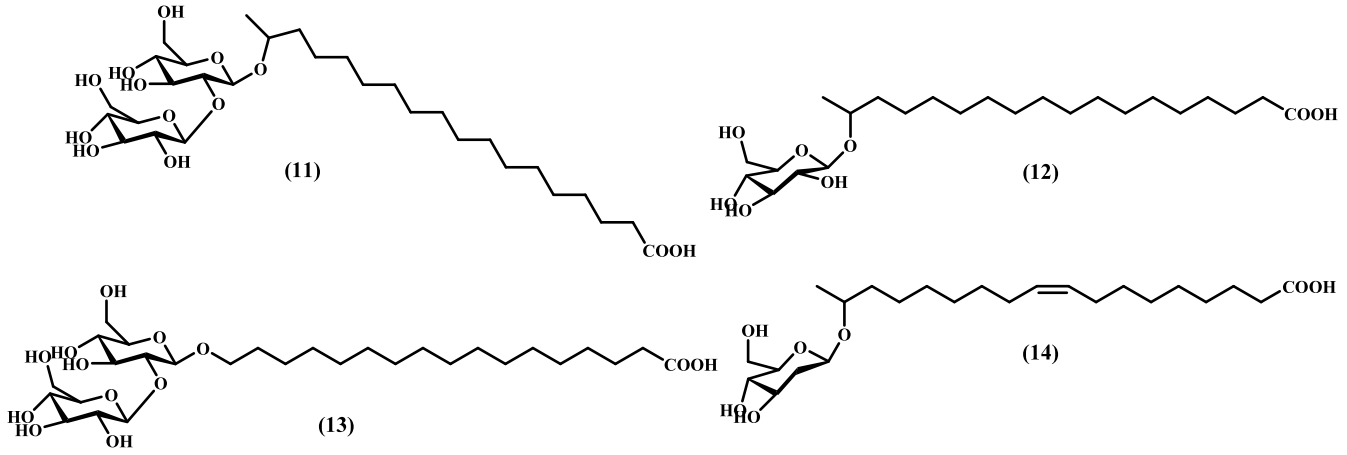


**Figure 9.** Structures representing glycolipid gelators based on renewable sources.

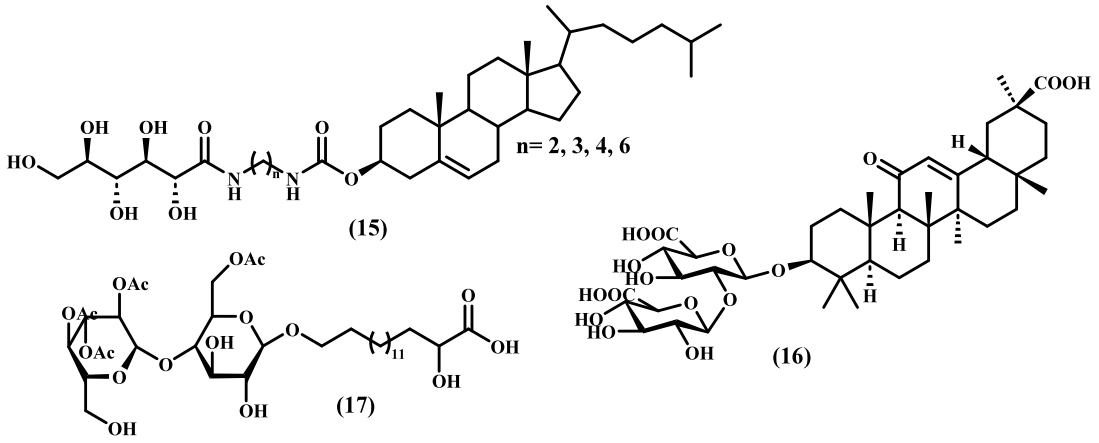


**Figure 10.** Structures representing glycolipid gelators based on renewable sources.

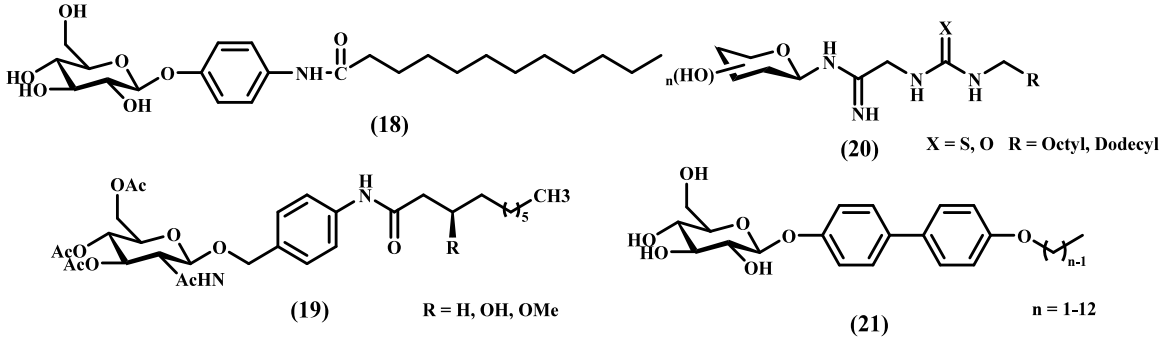


**Figure 11.** Structures representing glycolipid gelators based on monosaccharides.

Overall, in the case of amphiphilic lipid molecules, the self-assembly into diverse morphologies, including micelles, vesicles, fibers, and networks, is dependent upon factors such as structure, conditions, concentration, pH, and temperature.[56,63] This intrinsic property has been used for the construction of gels with adjustable properties and functionalities. This gelation process embraces a delicate balance between hydrophobic and hydrophilic interactions, as well as specific molecular interactions. Structural modifications in the amphiphile's molecular structure led to varied forms of self-assembled structures.[64,65] These soft materials, derived from amphiphiles with multiple functional groups, display mechanically tunable and multistimuli-responsive behavior, thereby making them promising for biomedical applications. More detailed explanations with proper examples giving perspective on the structure−property relationship of gelators are provided in upcoming sections.

## 4. GLYCOLIPID-BASED GELATORS

Glycolipids represent amphiphilic molecules comprised of a hydrophilic sugar headgroup and a hydrophobic lipid tail. Glycolipids sourced from renewable materials emerge as an environmentally sustainable and compelling alternative across various applications.[66,67] This class of compounds offers distinct advantages because of its cost-effective raw materials, sustainability, and versatile multifunctional molecular structures.


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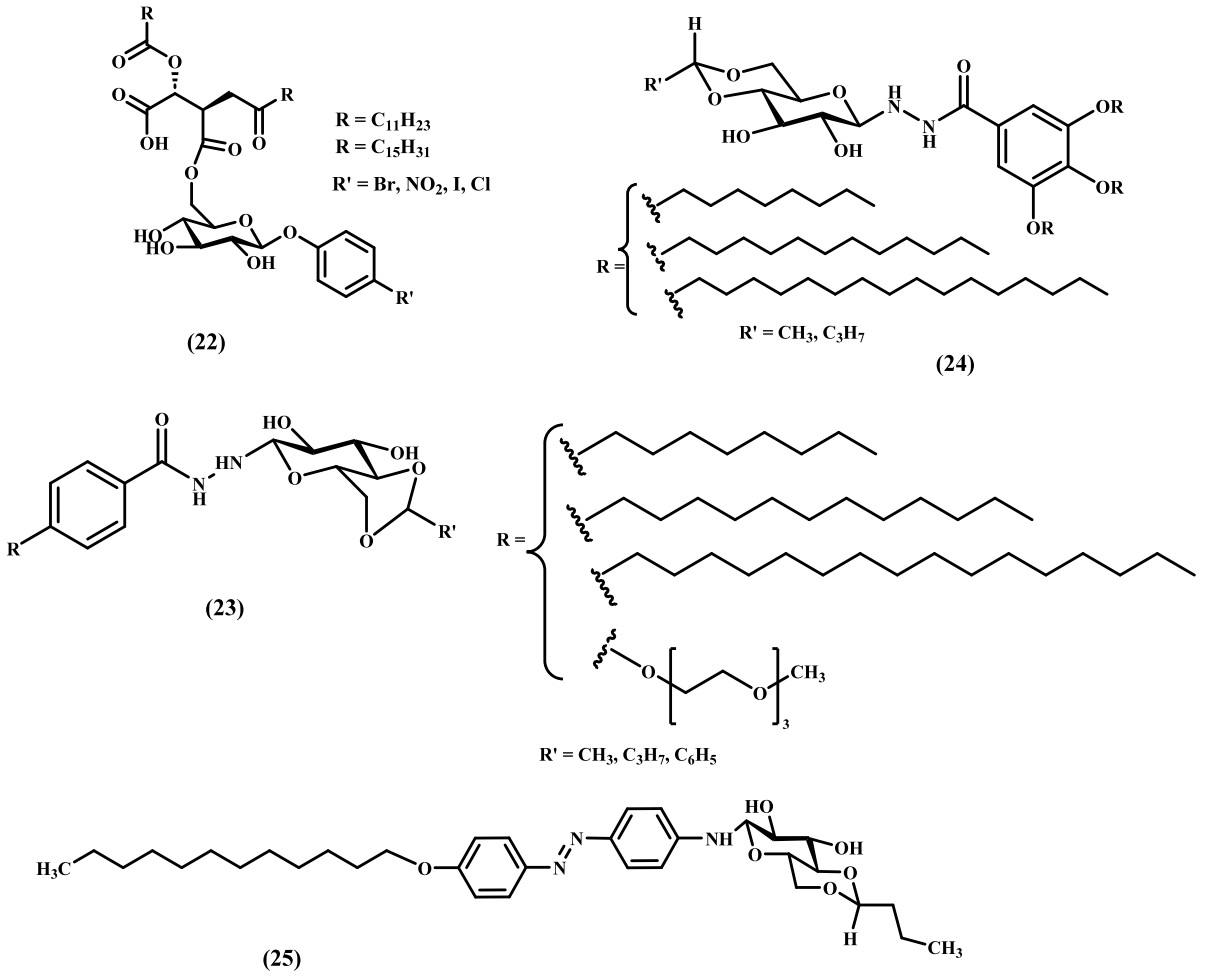


**Figure 12.** Structures representing glycolipid gelators based on monosaccharides.

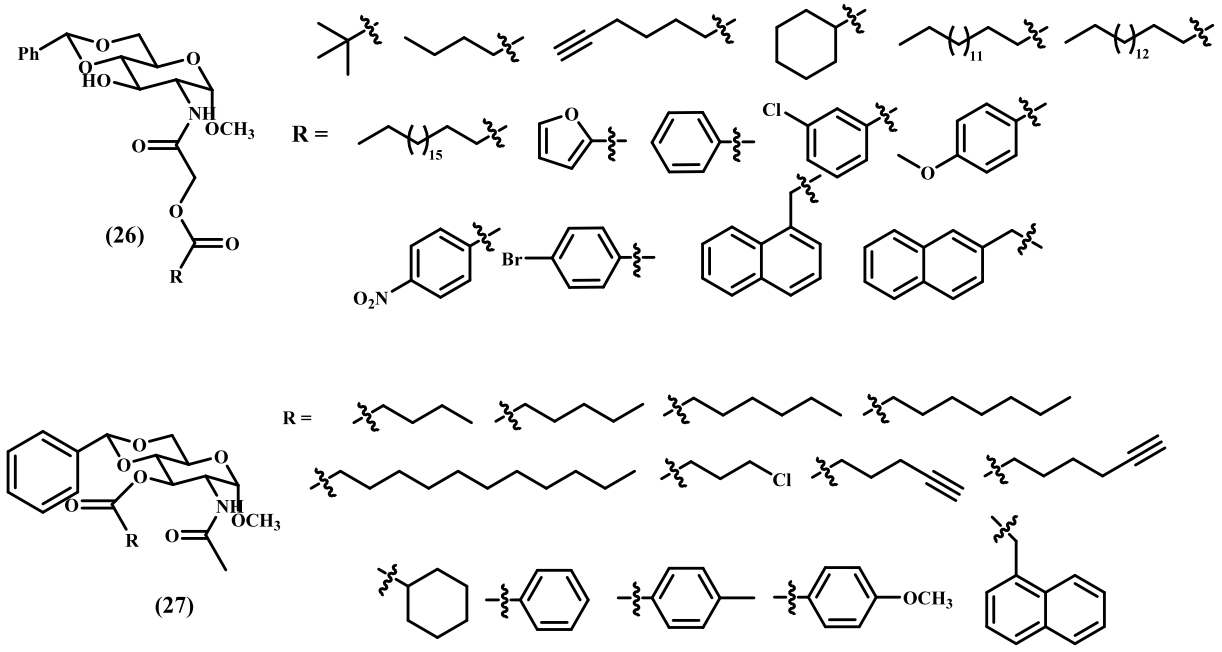


**Figure 13.** Structures representing glycolipid gelators based on monosaccharides.

Glycolipids crafted with specific designs have gained significant attention for biological applications.[68,69] Notably, the development of multifunctional architectures using sugar-derived gelators has become a focal point of interest.



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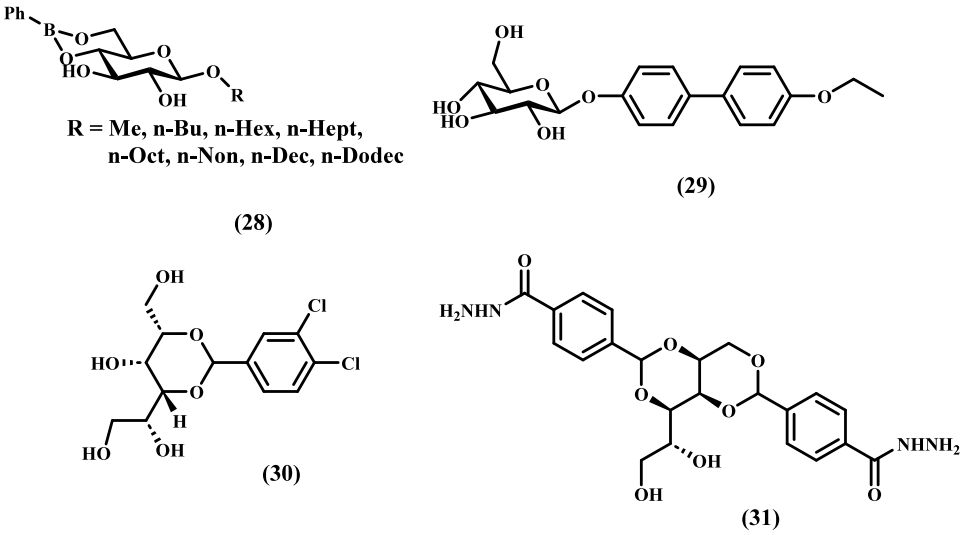


**Figure 14.** Structures representing glycolipid gelators based on monosaccharides.

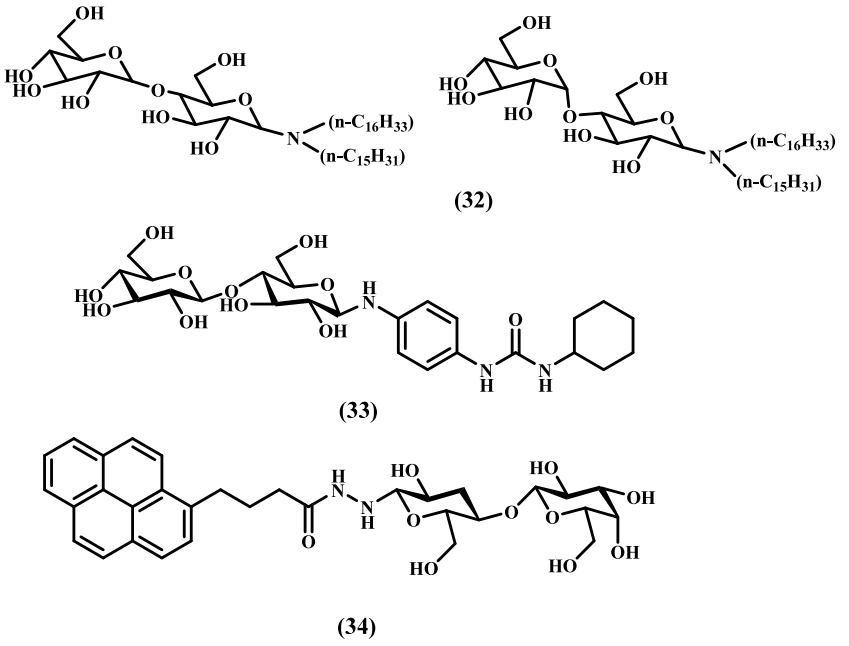


**Figure 15.** Structures representing glycolipid gelators based on disaccharides.

Given the amenability of carbohydrates to generate various classes of self-assembled soft materials with extensive applications, our focus is on glycolipid-based gelators. To date, a dedicated review focusing specifically on glycolipid gelators has evidently been absent from the literature. Recognizing this notable research gap, we decided to present a systematic analysis of glycolipid-based gelators to fill this void. To date, a large number of reviews are available in the literature featuring glycolipid gelators as one of the subsections explaining their several important properties.[22−24,29,70,71] In the provided articles, glycolipid-based gelators are regarded as merely one subset within the broader category of sugar-derived gelators, which may not fully encompass their significance. Therefore, the main purpose of this review is to bring together a detailed discussion of gelators based on glycolipids only. This review will provide easier access to the consolidated and existing knowledge exclusively on glycolipid gelators. It will also guide and provide an opportunity to identify the gaps, emerging trends, and inconsistencies in this field. Overall, this review will not only fulfill an unmet need in the scientific literature but also have far-reaching implications for advancing knowledge and driving practical applications.

On the basis of critical consideration of the literature, we have systematically classified glycolipid gelators into distinct categories guided by their specific structural specifications. Special emphasis on the hydrophilic sugar part in the design strategy of glycolipids is given. The justification for this classification can be stated as (a) structural diversity of sugar with numerous possible conformations, (b) crucial role of sugar in many biological activities, (c) rational design and synthesis strategies, (d) easy functional group modifications to achieve specific applications, etc. To facilitate the rational design of glycolipid-based gelators, it is beneficial to identify common themes prevalent in the existing literature. In the upcoming sections, different categories, such as glycolipids derived from renewable sources, glycolipid gelators based on monosacchar-


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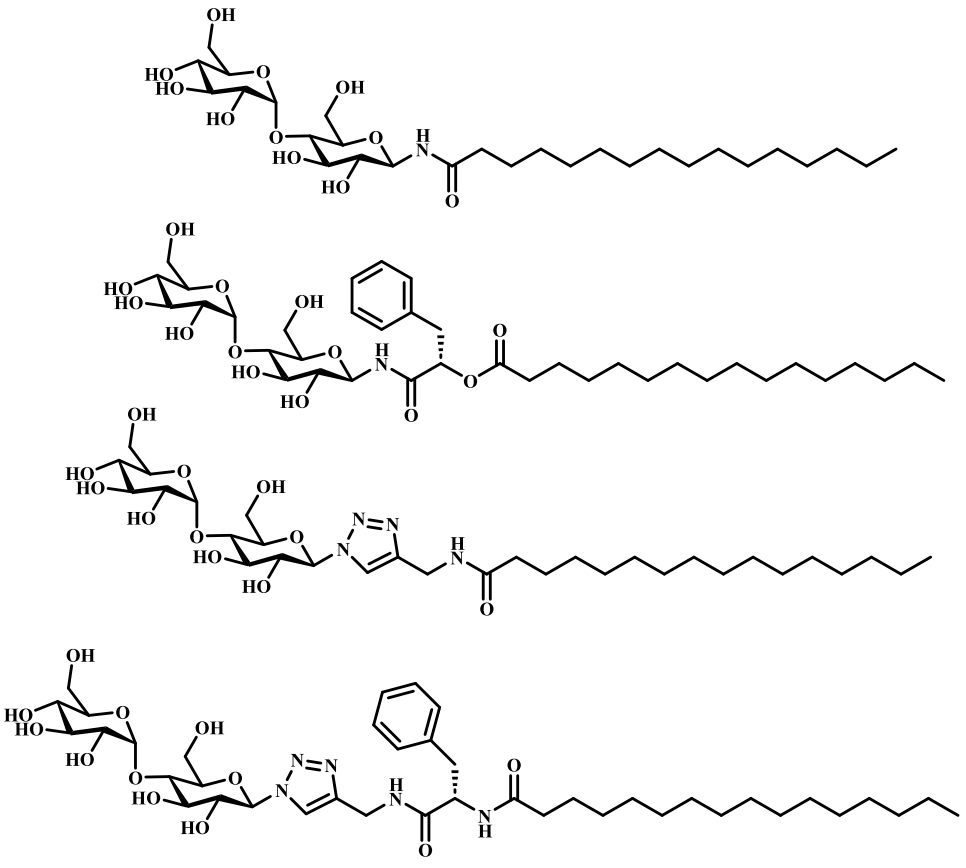

(35)

**Figure 16.** Structures representing glycolipid gelators based on disaccharides.

ides, disaccharides, derivatized sugars, bolaamphiphiles, and some miscellaneous glycolipid gelators, will be discussed. For the purpose of this review, it is not feasible to cover the other practical factors related to gel properties, such as minimum gelation concentrations, micrographs, melting temperatures, etc. (these details can be found in the cited references).

**4.1. Glycolipid Gelators Based on Renewable Sources.** The development of glycolipid gelators on the basis of renewable sources represents a promising avenue in materials science. John and co-workers pursued various methodologies to develop hydrogelators derived from sustainable sources.[29,66] By employing enzymatic synthesis, they successfully created a biobased amphiphile from the naturally occurring sugar-based molecule, amygdalin. Their study revealed that this enzymatic process triggered the controlled release of natural drug curcumin [Figure 5, (**1**)].[72] Additionally, they have also reported the synthesis of amphiphilic glycolipids sourced from cashew nut shell liquid (cardanol), a plant-based raw material [Figure 5, (**2**)]. The self-assembly of these glycolipids yielded soft nanoarchitectures that include nanotubes, nanofibers, supramolecular gels, and liquid crystals.[61,73,74] These self-assembled morphologies were further implemented to generate high-axial-ratio nanostructures (HARNs) and as candidates for a cytomimetic tubule. Notably, glycolipids demonstrated the formation of transparent thermoreversible gels in water−alcohol mixtures and various organic solvents, with their properties strongly affected by the unsaturation of the fatty alkyl chain.[75]

This group also modified the structures of these cardanol-derivatized lipids by fusing them with other moieties. Another study illustrates that long-chain phenyl glucoside can give rise to twisted nanofibers, helical ribbons, and nanotubular structures with a specific morphology depending on the presence of unsaturated double bonds. These findings represent the initial investigation into the systematic effects of *cis* double bond units in hydrophobic segments on the self-assembled morphologies [Figure 6, (**3**)].[48] They also studied the structural prerequisites necessary for the self-assembly of amphiphilic monomers into intricately organized nanotubes. This knowledge holds potential for designing single-chain amphiphiles capable of forming nanostructures with high axial ratios from simple molecules. Additionally, these designed molecules may include molecular recognition groups that enable monitoring of the chemical selectivity of supramolecular aggregates toward guest binding [Figure 6, (**4**)].[76]

Nagarajan and colleagues successfully produced glycolipids from sustainable sources, namely cashew nut shell liquid and monosaccharides, and achieved commendable yields [Figure 7, (**5**)].[77] Their investigation focused on the self-assembly of such types of glycolipids by forming gels in hydrophobic solvents and vegetable oils while also demonstrating the formation of foam in water. The researchers explored the potential applications of such self-assembled glycolipids with slight structural modification in examining their ability to disrupt preformed biofilms across several pathogens [Figure 7, (**6**)].[68] Further, they have synthesized three sets of amphiphilic compounds using cashew nut shell liquid and $\delta$-gluconolactone. These glycolipids also displayed biofilm inhibition and antimicrobial activity against bacterial pathogens [Figure 7, (**7**)].[67]



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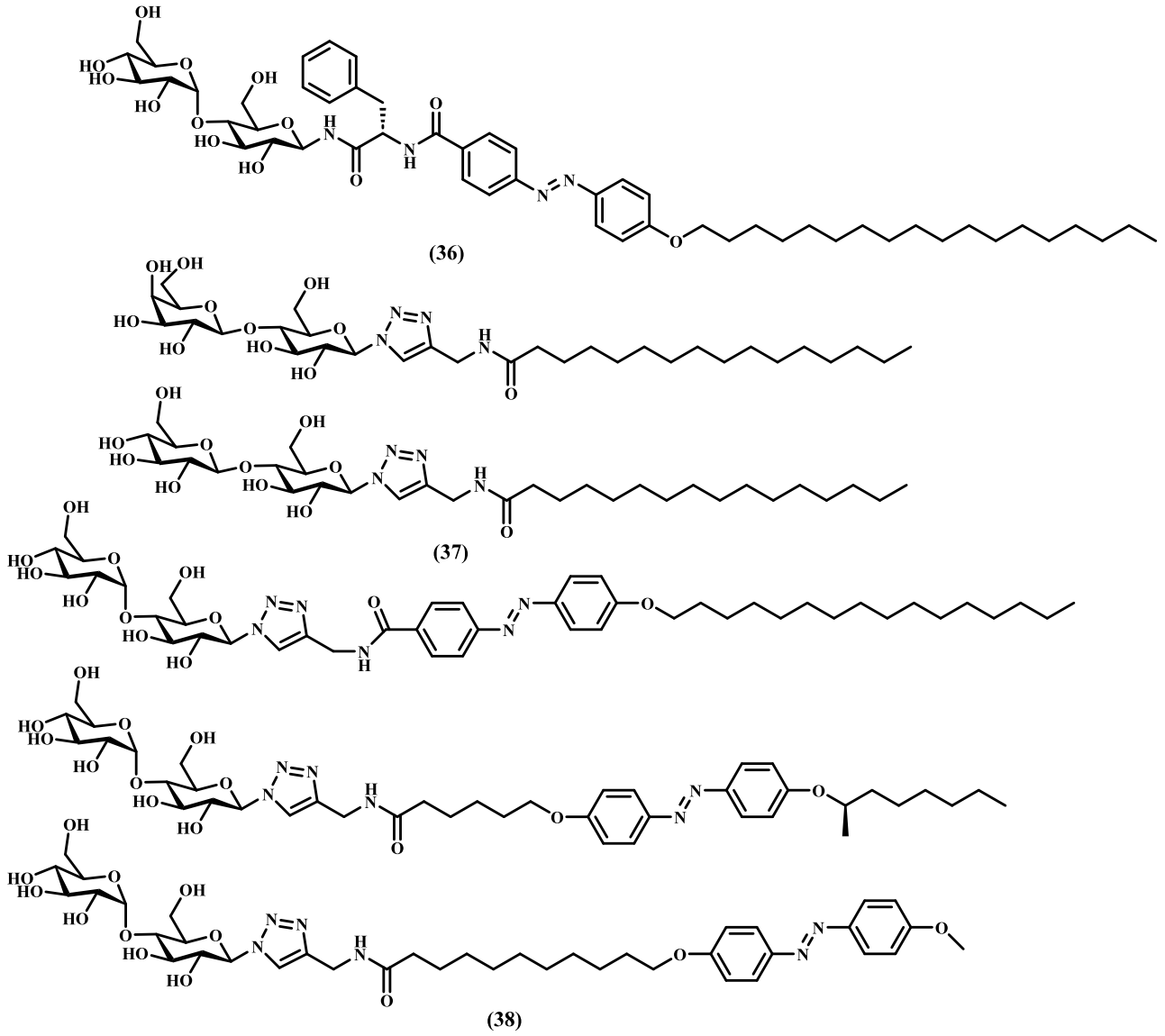


**Figure 17.** Structures representing glycolipid gelators based on disaccharides.

Furthermore, the *in situ* synthesis of gold nanoparticles utilizing ascorbic acid-based amphiphiles with a sugar-based building block was investigated. John et al. have also discussed the self-assembling properties of these amphiphiles to give hydro/organogels and liquid crystals [Figure 8, (**8**)].[78] Nandi and colleagues formulated a series of innovative lipid-modified derivatives of vitamin C, which constituted a fusion of the fatty acids and hydroxycarboxylic acids (such as tartaric acid and malic acid) [Figure 8, (**9**)].[79] Amphiphiles of tartaric acid with C14 and C16 chain lengths and malic acid with C16 chain lengths displayed excellent hydrogelation at room temperature. This research revealed that the gelation behavior and stability in water were significantly influenced by the alkyl chain length of the hydrocarbon. In another study, the structure and rheological properties of gels formed from water dispersions of a surfactant derived from vitamin C (ascorbyl-6-*O*-dodecanoate) were examined using SAXS and rheology experiments [Figure 8, (**10**)].[45]

In another class, the process of pH-induced fibrillation of the stearic derivative of acidic sophorolipids was elucidated by Cuvier et al. [Figure 9, (**11**)].[80] Further, Ben Messaoud et al. have investigated the hydrogel properties of stearic acid sophorolipid, a glycolipid of microbial origin, driven by pH changes accompanied by a micelle-to-twisted ribbon phase transition of this compound around pH 7.4.[36] A novel glucolipid, derived in significant quantities from glucose and vegetable oils through microbial fermentation of the engineered yeast strain *Starmerella bombicola* ΔugtB1, can create lamellar rheo-thinning hydrogels in water within a pH range of 5 to 7.5 and ionic strength ranging from 10 to 500 mM [Figure 9, (**12**)].[52] In another report, the connection between structural and elastic characteristics was examined through *in situ* rheo-SAXS analysis of a lipid lamellar hydrogel comprised of this novel pH-responsive glucolipid.[53]

Baccile and colleagues investigated the self-assembly characteristics of nonacetylated palmitic acid sophorolipids (SLC16:0). It was observed that nanofibers emerge at pH levels below 6, which marks a transition from micelles to fibers. This study demonstrates that palmitic acid C16:0 sophorolipids exhibit spontaneous micelle formation at pH above 7 and fiber formation at pH below 6 [Figure 9, (**13**)].[81] Furthermore, the authors synthesized a microbial glycolipid (sophorolipid)


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*ACS Omega* 2024, 9, 25513−25538

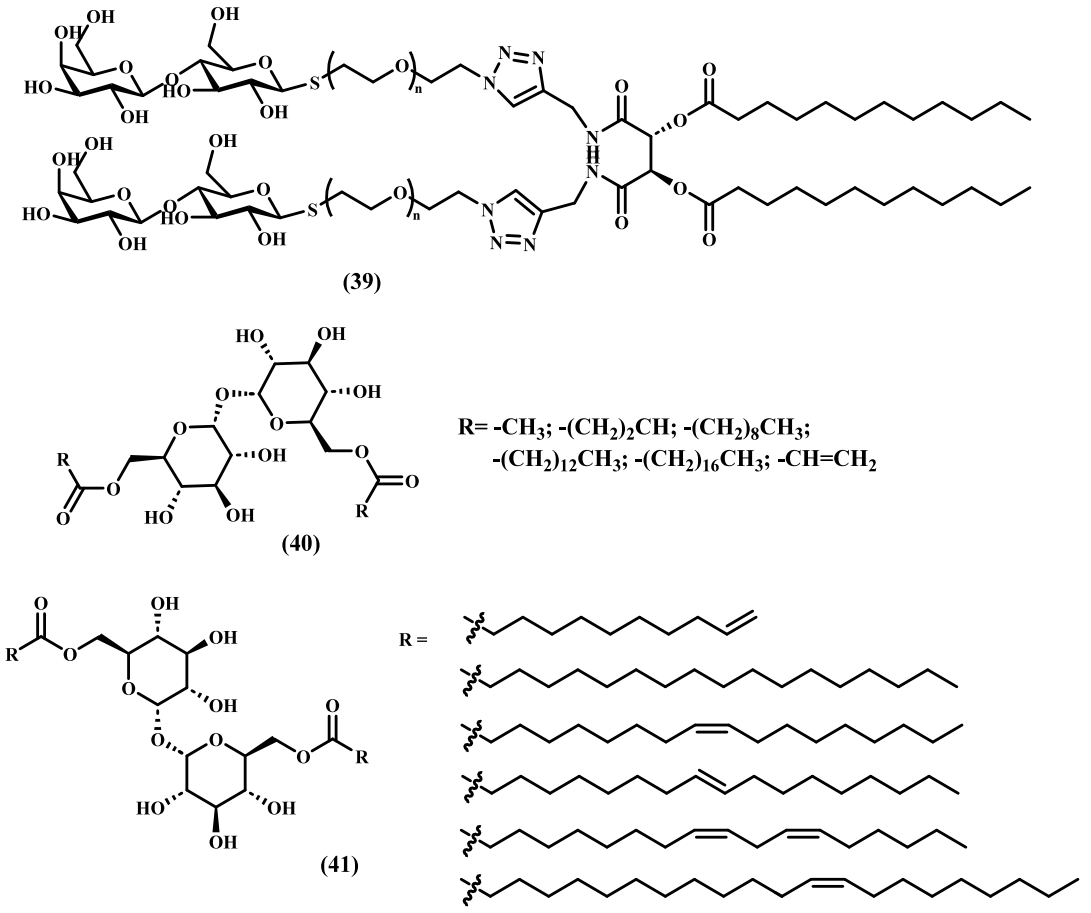


**Figure 18.** Structures representing glycolipid gelators based on disaccharides.

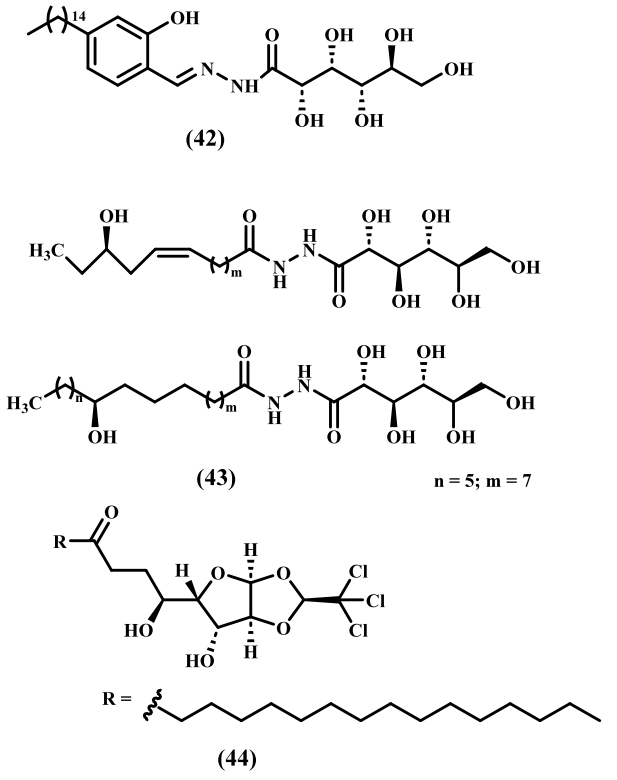


**Figure 19.** Structures representing glycolipid gelators based on derivatized sugar.

described in their study, which comprises a glucose group attached to a C18:1-*cis* fatty acid and is obtained through the fermentation of *S. bombicola* ΔugtB1 [Figure 9, (**14**)]. Within the pH range of 5 to 7, it exhibits vesicle formation, and beyond pH 7, it undergoes a transition into a micellar phase. The introduction of free metal ions ($Cr^{2+}$, $Mn^{2+}$, $Ca^{2+}$, and $Ag^{+}$) into the same micellar phase unexpectedly triggers the formation of hydrogels characterized by a fibrillar structure.[54] The identical glycolipid compound exhibited the capability to generate a metallogel through cation complexation in water, thereby effectively immobilizing heavy metals within the gel phase. This mechanism facilitates the removal of cobalt (up to 95%) and significant percentages for other metals, including $Cu^{2+}$, $Ni^{2+}$, and $Cr^{2+}$.[82,83] Additionally, they successfully developed interpenetrated hydrogels composed of biosurfactant and biopolymer by utilizing biobased glycolipid amphiphiles and biopolymers. This highlights the feasibility of creating functional hydrogels with elastic properties that respond *in situ* to external stimuli, all derived from entirely sustainable components.[84]

Four efficient LMWGs are reported from the cholesterol and sugar components. Gelation experiments conducted in different solvents revealed that even a slight modification in the linker length could result in a significant alteration in the gelation characteristics and properties of the compounds. Additionally, these xylene gel systems demonstrated film-forming capabilities utilizing a straightforward solution casting technique [Figure 10, (**15**)].[85]

The self-assembly behavior of glycyrrhizic acid (GA), a naturally occurring sweetening agent in water, was investigated


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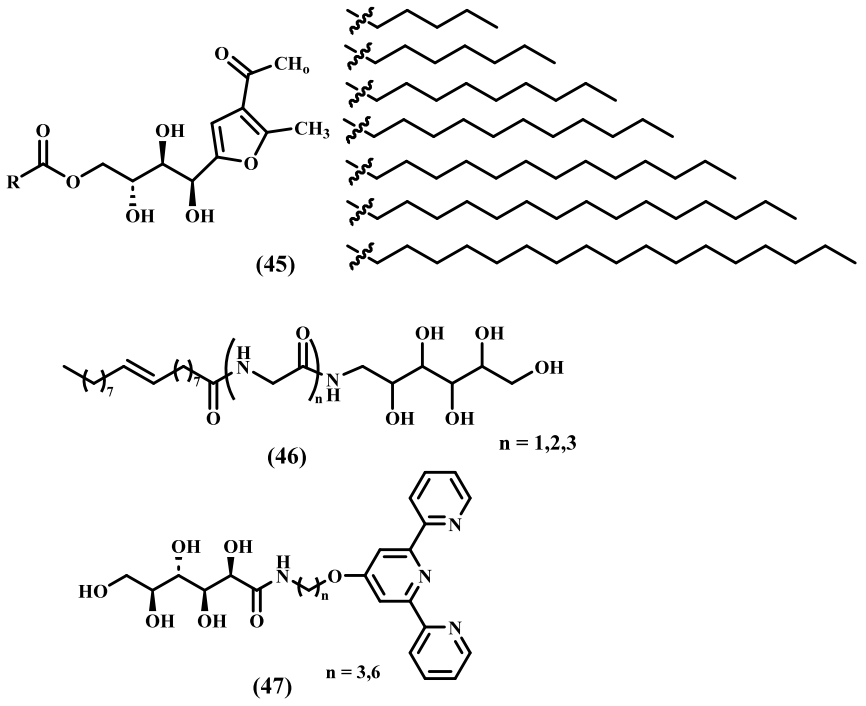


**Figure 20.** Structures representing glycolipid gelators based on derivatized sugar.

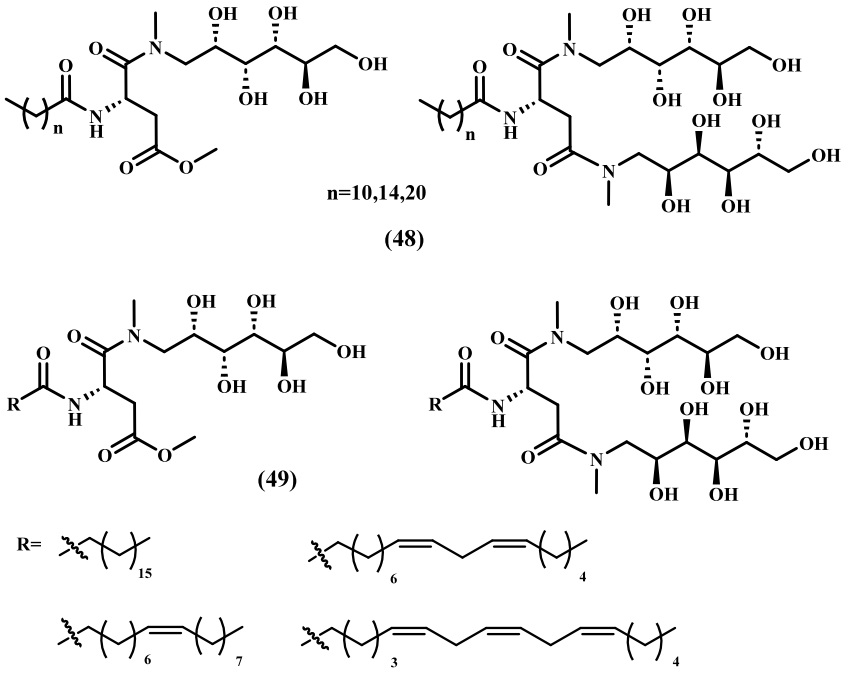


**Figure 21.** Structures representing glycolipid gelators based on a derivatized sugar.

by using small-angle X-ray scattering and microscopic techniques. Twofold and threefold hybrids were fabricated by incorporating graphene oxide (GO) and *in situ* synthesized gold nanoparticles (Au NPs) into the hydrogels and were implemented for catalytic applications [Figure 10, (**16**)].[86] In another report, the adsorption properties at the air−water interface and self-assembly in a solution of GA were studied using neutron reflectivity and small-angle neutron scattering techniques. Both nongelling and gelling conditions were explored, which revealed that gelation has minimal influence on the adsorption process.[87] Yang and co-workers' investigations strongly indicate that the self-assembled GA nanofibrils hold promise as an outstanding building material for the development and production of responsive supramolecular materials and multiphase soft matter.[88,89] In another work, an innovative bioactive hybrid hydrogel based on GA demonstrated promise as a dressing material to facilitate the healing of full-thickness wounds and bacterial-infected wounds.[90]

Imura et al. reported cellobiose lipids (CLs), bolaform glycolipid biosurfactants, derived from natural resources through yeast fermentation. Their study explored the gelation characteristics of CL in various solvents by employing multiple


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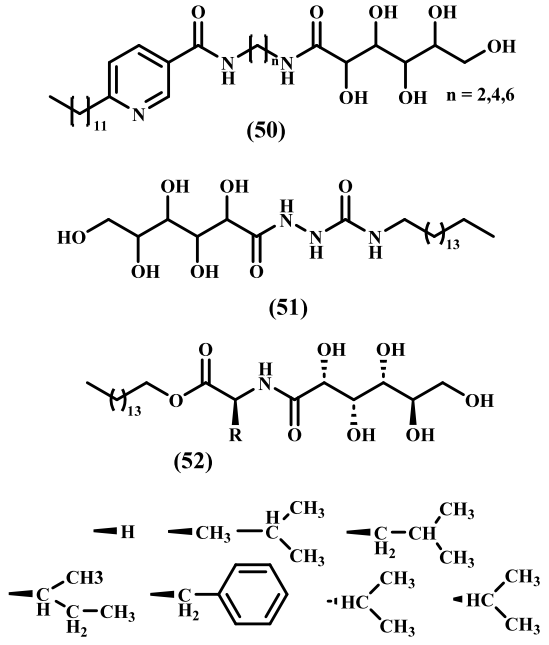


**Figure 22.** Structures representing glycolipid gelators based on derivatized sugar.

techniques, such as rheology and atomic force microscopy (AFM) [Figure 10, (**17**)].[91] In a separate study, the sodium salts of CLs (CLNa) were synthesized to enhance the aqueous solubility, and their surface properties and gelation behavior were investigated. Given that these CLNa aqueous gels possess fungicidal activity, they hold potential as innovative multifunctional soft materials applicable in the food and cosmetic industries.[92]

**4.2. Glycolipid Gelators Based on Monosaccharides.** Carbohydrates, apart from serving as hydrogen-bond-forming segments in gelators, offer the advantage of introducing diverse stereogenic centers into gelators by selectively choosing from a saccharide library. Derivatization of glycogen (C-derivatized or O-derivatized) to form an amphiphile is also an important principle while designing a glycolipid gelator.[23,93] Exploring the arena of monosaccharide-based glycolipid gelators, a deliberately synthesized gelator was studied for its gelation capacity in both organic solvents and water [Figure 11, (**18**)].[94] The work extended to identifying sugars and suitable hydrophobic groups to potentially uncover highly effective amphiphilic gelators.

The synthesis of a glycolipid-based gelator and its methoxy and hydroxy derivatives was investigated to study the impact of different modes of supramolecular assembly, such as intermolecular hydrogen bonding, intramolecular hydrogen bonding, and a combination of both [Figure 11, (**19**)].[95] The work underscores that integrating intramolecular hydrogen bonds via *β*-hydroxy fatty acid moieties in the structure of glycolipid-based gelators provides a straightforward approach to enhance the anion responsiveness. New glycolipids featuring thiourea and urea-linkers were synthesized as LMWGs by reacting glycosyl aminoacetamides with alkyl isothiocyanates and isocyanates. The study investigated the impact of the linker groups on the self-assembly properties of these compounds [Figure 11, (**20**)].[96]

Cui et al. designed an amphiphilic molecule featuring a hydrophilic and chiral glucoside unit alongside a hydrophobic biphenyl moiety with butoxy tails and investigated it for its gelling capabilities. The compound demonstrated efficient gelation across various solvent systems, encompassing water. The resulting gel morphologies were meticulously examined and were observed to exhibit pronounced dependence on the solvent nature influenced by diverse solvation effects and intermolecular interaction mechanisms.[62] Furthermore, a set of sugar-appended glucoside organogelators was synthesized to investigate the influence of chain length on their gelation behavior and chiral expression capabilities within gels [Figure 11, (**21**)].[97]

Das and co-workers synthesized the collection of glycolipid derivatives derived from *N*-glycosylamines, and their organogelation properties were examined. The study revealed that gelation primarily occurred in aliphatic solvents with a minimum gelation concentration of 0.8% (w/v), a phenomenon ascribed to the extended alkyl chains present in glycolipids [Figure 12, (**22**)].[98] Further, they have reported a class of sugar benzohydrazide derivatives with a long alkyl chain. Self-assembly of organogels formulated using designed gelators was studied in different solvents [Figure 12, (**23**)].[99] In their other work, *N*-glycosylamine derivatives based on 3,4,5-tri-*O*-benzohydrazide were reported to have good gelation properties in oils, as well as many solvents. Further, these gelators also displayed the property of phase-selective gelation for several oils and organic solvents in the presence of a water medium, along with the dye removal capacity [Figure 12, (**24**)].[100] Gelators based on sugar derivatives with an azobenzene group and long alkyl chain showed photoinduced gel−sol transition with irradiation by UV light and visible light. Accompanied with phase-selective gelation, these gelators also removed cationic dyes with high efficiency from polluted water [Figure 12, (**25**)].[101]

Wang and colleagues synthesized and characterized 15 glycolipids derived from *N*-acetyl-D-glucosamine. These glycolipids featured an amide with diverse ester functional groups, which encompassed aliphatic derivatives with differing chain lengths and aromatic derivatives. The intentional design of these gelators positions them as potential stimuli-responsive smart materials offering controlled release properties for various applications [Figure 13, (**26**)].[102] In another report, authors explored a series of alkyl and aromatic ester derivatives of sugar. The alkyl ester derivatives were observed to be effective gelators for oils and other mixtures of solvents compared with the aromatic ones. The gelation behavior of reported molecules displayed the dependency of functionalization at a particular position that can provide a new class of gelators [Figure 13, (**27**)].[103] Furthermore, to understand the structural requirement for gelation, they successfully synthesized two sets of carbamates using basic monosaccharide headgroups. Their investigations revealed distinct structural preferences for gelation between the O-linked carbamate derivatives and their ester counterparts. Unlike the ester derivatives, it was observed that the presence of a terminal acetylene group is not essential for efficient gelation in carbamates.[93]

The same group is actively engaged in investigating the various approaches to synthesize a diverse array of LMWGs derived from methyl 4,6-*O*-benzylidene-*α*-D-glucopyranose through straightforward synthetic procedures. In their study, 18 novel glycolipids incorporating 4,6-*O*-benzylidene acetal-protected D-glucosamide were synthesized and thoroughly characterized. The self-assembly behavior of these compounds was assessed in a range of organic solvents, aqueous solutions, and water.[104] The design of glycolipid-based gelators can be altered by modifying their structure. In another report,


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ACS Omega 2024, 9, 25513−25538

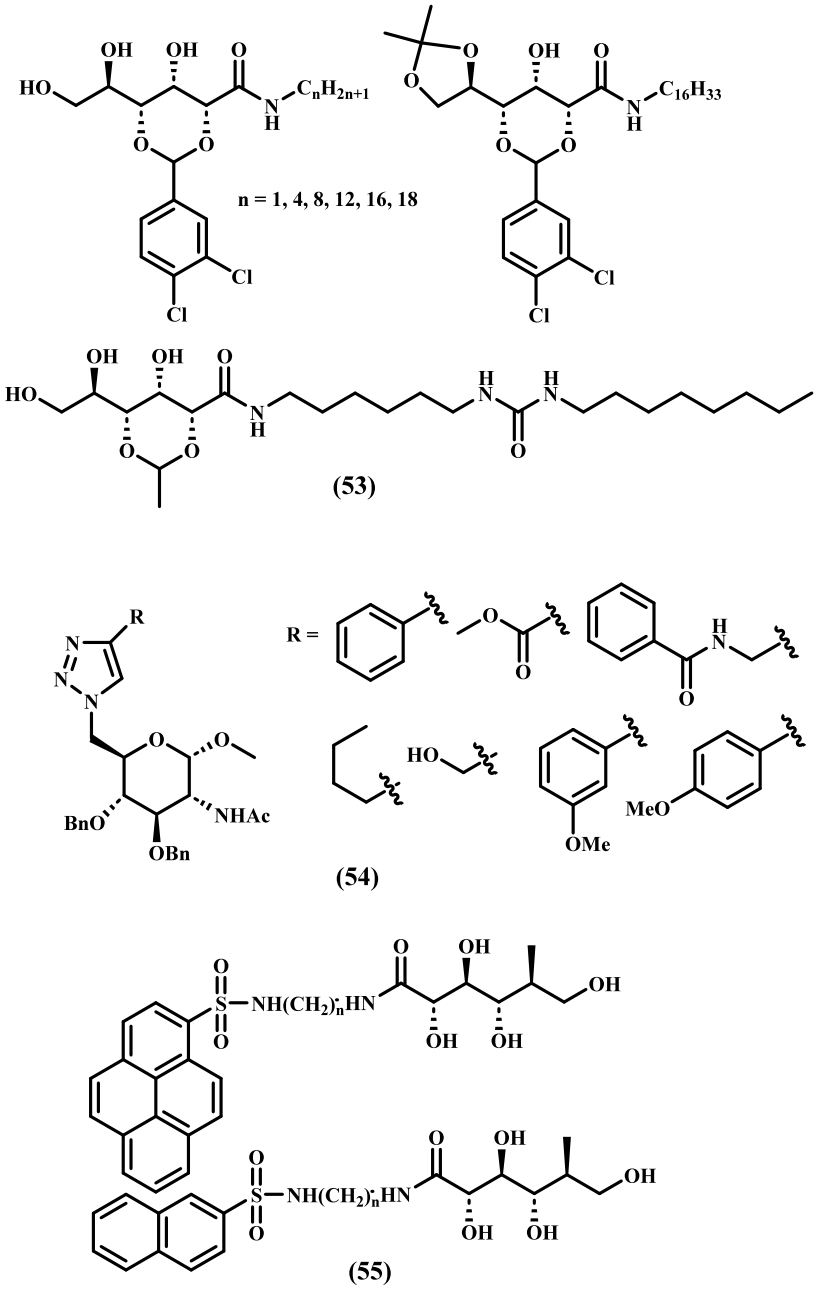


**Figure 23.** Structures representing glycolipid gelators based on derivatized sugar.

glycolipid-based gelators were formulated by incorporating a triazole functional group. A series of glycolipids was prepared, and their gelation and self-assembling characteristics were studied, along with the effect of structural variations. Further, these hydrogels were implemented to study the controlled release of chloramphenicol and entrapment of dye.[105,106]

A series of phenylboronic esters-based glycolipids were prepared using phenylboronic acid and alkylglucosides in a single step. After evaluating their gelation behavior, it was observed that these soft materials can be used for controlled release and drug delivery [Figure 14, (**28**)].[107] A sugar-based glucoside gelator was checked for its gelation in various solvents. The structural transition from gel to crystal was observed in the mixture of 1,4-dioxane and water. Also, the transition to the gel crystal could be modulated by varying the solvent composition [Figure 14, (**29**)].[108] A new sorbitol based-LMWG was designed, and the salt effect on the gelation of this molecule was studied by Li et al. Because of the addition of salt, the process of gelation was accelerated and changed the gel morphology of the gel to long fibers from globular [Figure 14, (**30**)].[109]

The Smith group reported the formulation of sorbitol-derived LMWG, DBS-CONHNH$_2$ [Figure 14, (**31**)].[110] They combined this LMWG with polymeric gelators, such as calcium alginate and agarose, to get a hybrid gel. This interpenetrating network with a self-assembled LMWG was used to reduce palladium to Pd nanoparticles. These nanoparticles were used to catalyze Suzuki−Miyaura reaction.[13,111] In another report, they combined this LMWG with calcium alginate having a pH-triggered assembly to obtain the hybrid gel beads. These gel beads incorporated with silver nanoparticles can be employed


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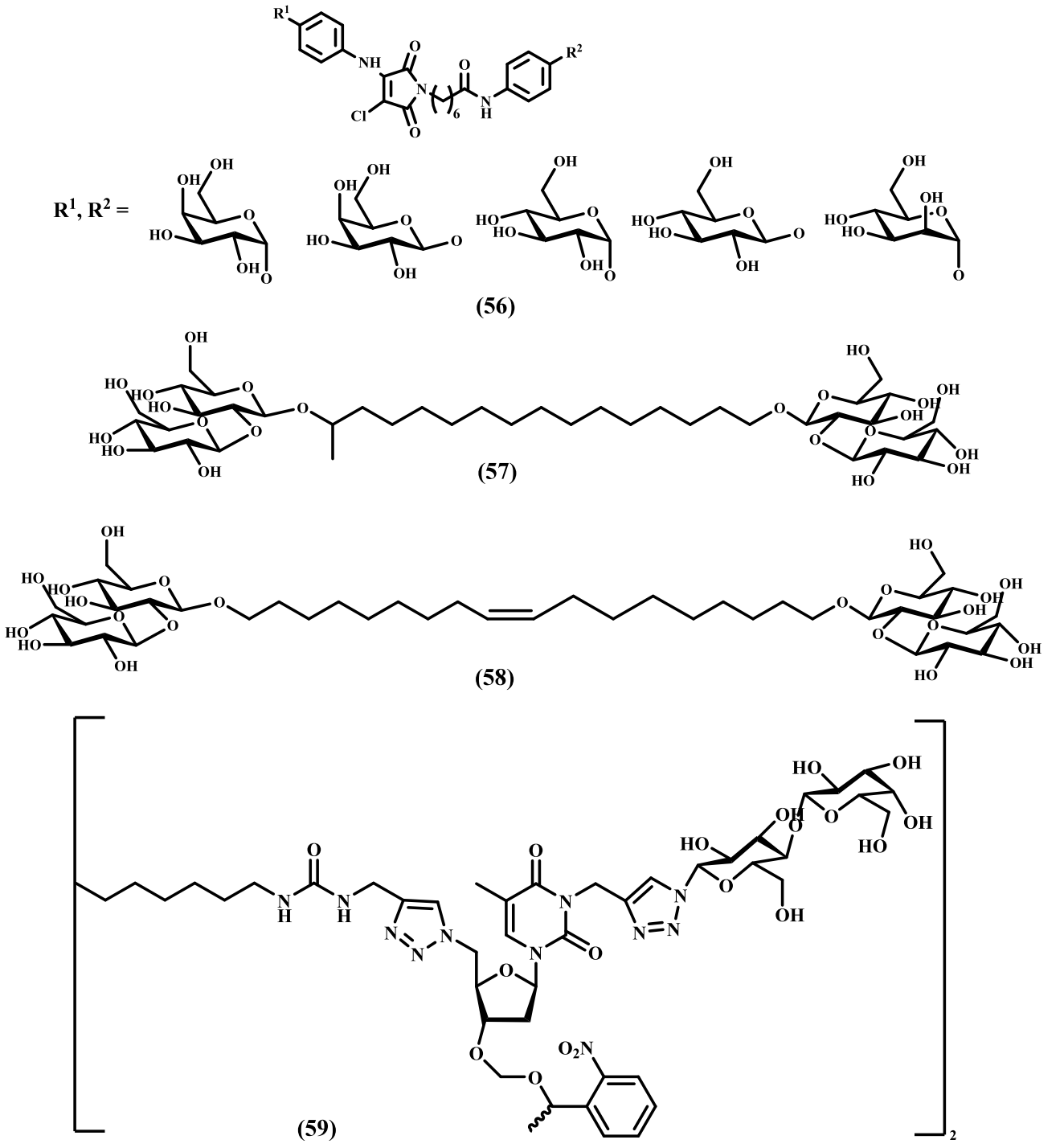


**Figure 24.** Structures representing glycolipid gelators containing bolaamphiphilic glycolipids.

for antibacterial properties and are compatible with human stem cells.[112]

**4.3. Glycolipid Gelators Based on Disaccharides.** In a preliminary study, Bhattacharya and colleagues showcased the facile hydrogelation achieved using *N*-alkyl disaccharide amphiphiles derived from D-maltose and D-lactose [Figure 15, (**32**)].[113] Among the six disaccharides examined, certain variations resulted in hydrogel formation, while others did not exhibit gelation. The low minimum gelation concentration values observed for the *N*-alkyl disaccharide amphiphiles were ascribed to the occurrence of substantial interlamellar spaces in which water molecules were immobilized through capillary forces. Furthermore, the group reported efficient gelation behavior for fatty acid amides in both aliphatic and aromatic hydrocarbon solvents.[114]

An amphiphilic molecule incorporating a hydrophilic lactose group was synthesized as a low-molecular-weight hydrogelator, which resulted in the formation of a supramolecular transparent hydrogel. The enzymatic hydrolysis of lactose moiety, facilitated by $\beta$-galactosidase, showcased gel-to-sol phase transition in supramolecular hydrogel [Figure 15, (**33**)].[115] A pyrene-based amphiphile with lactose undergoes self-assembly in aqueous media, which resulted in the formation of an injectable hydrogel. This amphiphile exhibits a preference for binding with cholera


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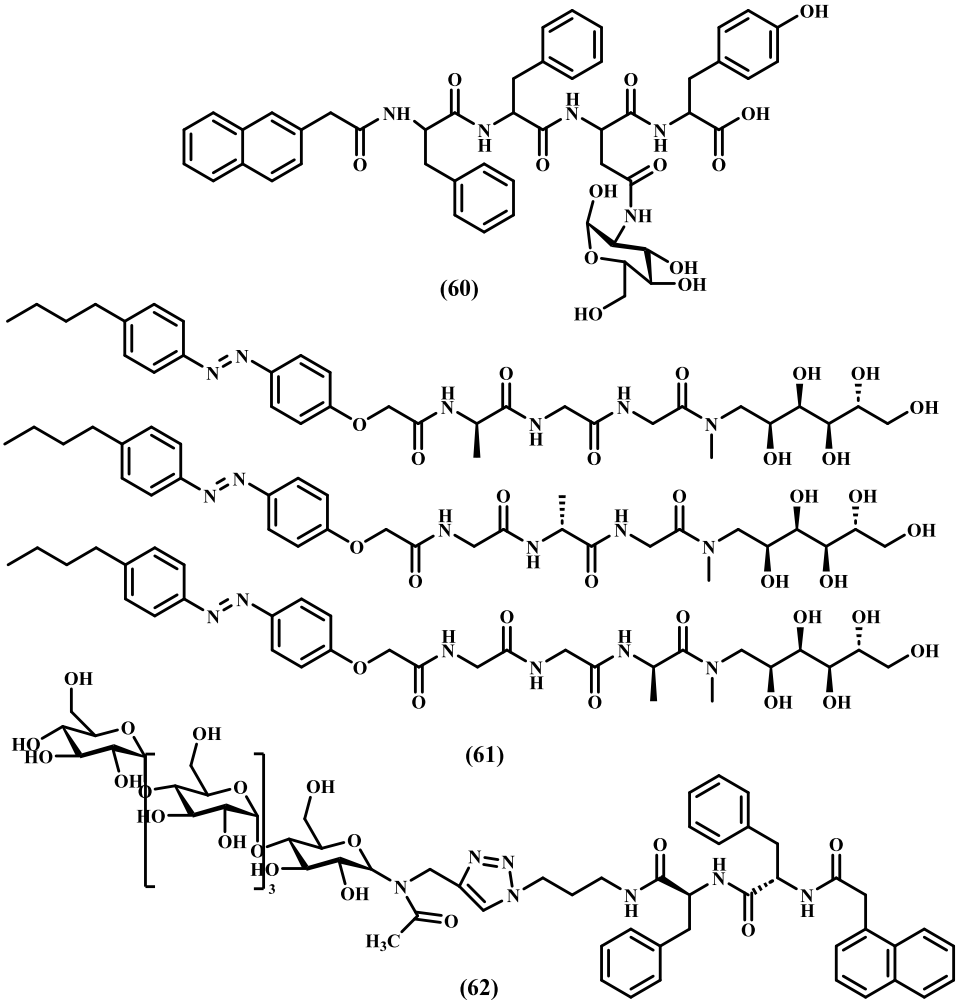


**Figure 25.** Structures representing miscellaneous glycolipid gelators.

toxin (CT) through its terminal galactose residue. As a result, it can be utilized for the selective detection of CT by manifesting a color-changing behavior [Figure 15, (**34**)].[116]

Oriol and colleagues synthesized amphiphilic glycolipids by connecting a maltose polar head to a long hydrophobic alkyl chain through either amidation or azide−alkyne cycloaddition catalyzed by copper [Figure 16, (**35**)]. The liquid crystalline properties of the amphiphiles were characterized. The study also investigated the impact of the core chemical structure of these glycolipids on their gelation behavior in water.[117] In the pursuit of discovering novel materials grounded in low-molecular-weight amphiphiles, they have synthesized a novel series of photoresponsive gelators. These gelators featured azobenzene as a photosensitive unit, D-maltose/poly(ethylene glycol) (PEG) as the hydrophilic polar head, and were linked via L-phenylalanine [Figure 17, (**36**)].[118] The gelation properties of both the final amphiphiles and intermediate molecules were investigated across various solvents. Notably, two of the materials demonstrated a gel-to-sol transition upon UV light irradiation followed by thermal *cis*−*trans* isomerization, then returned to a gel state at room temperature. Further, this group has explored glycolipid amphiphile gelators featuring disaccharides as polar head groups, which have been studied for their liquid crystalline and gel-forming properties [Figure 17, (**37**)].[119] Connecting with their previous work, a maltose-based glycolipid gelator with a photoactive azobenzene group in the hydrophobic chain was prepared. The self-assembled structures were characterized for their chiral properties [Figure 17, (**38**)].[120]

Cano et al. reported two thiolactose-based glycolipid amphiphiles with varying spacer lengths by a single ethylene glycol unit. Amphiphiles with a shorter linker only formed a hydrogel, which proves the impact of linker length. They were implemented to study their lectin binding ability [Figure 18, (**39**)].[121] Dordick et al. have proposed a biocatalytic approach for designing and synthesizing a new series of highly symmetrical trehalose diesters. The capability of longer-chain trehalose diesters to gel olive oil suggests their potential application as additives in food or cosmetics. Furthermore, the photopolymerization of diacrylate esters yields stable organo- and hydrogels and holds promise for diverse applications [Figure 18, (**40**)].[122] The Cramail group also synthesized trehalose diesters with different fatty acids with selective enzymatic transesterification and studied their gelation behavior in oils. It was observed that the gel properties were dependent on the type of fatty acid, as well as the composition of vegetable oil used [Figure 18, (**41**)].[123]

**4.4. Glycolipid Gelators Based on Derivatized Sugar.** Glycolipids based on the various forms of sugars with some modifications represent an efficient class of novel gelators. Nagarajan and co-workers developed trimethylamine sensor fabric through a stepwise self-assembly process utilizing


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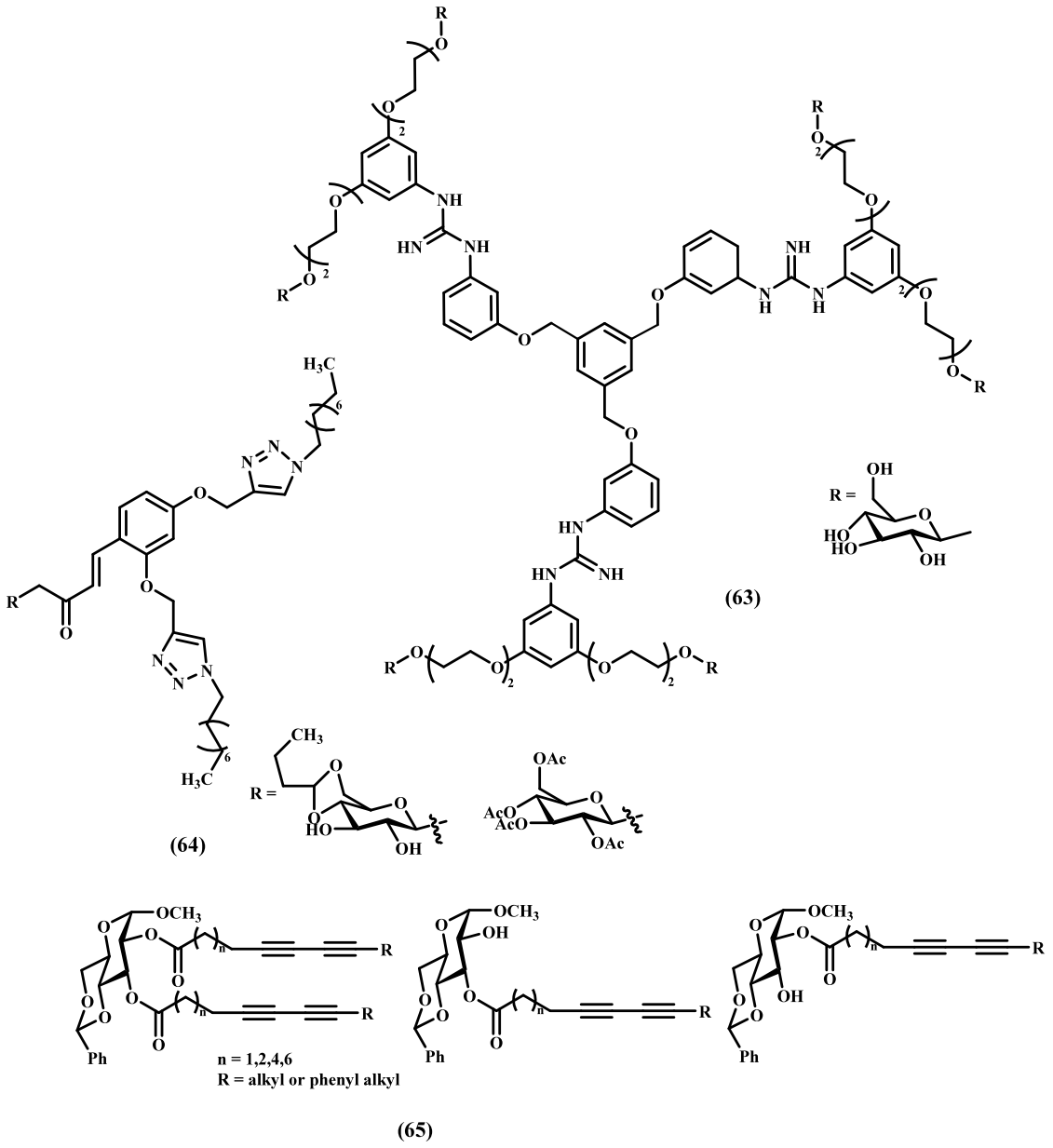


**Figure 26.** Structures representing miscellaneous glycolipid gelators.

glycolipids incorporating silver [Figure 19, (**42**)]. The comprehensive examination of the formation of a self-assembled supramolecular glycolipid-based gel, the interaction between the assembled structure and cotton fabric, and the elucidation of the sensing mechanism have been conducted.[124]

They further synthesized gelator molecules through a thoughtful amalgamation of $\delta$-gluconolactone and ricinoleic acid [Figure 19, (**43**)]. The resultant glycolipids demonstrated self-assembling capabilities within a diverse array of vegetable oils, as well as commercially relevant substrates, such as ethylene glycol, glycerol, and polyethylene glycol, facilitated by various intermolecular interactions leading to gel formation. The self-assembled organogel and oleogel disclosed in their study hold significant potential for applications in many areas, along with food, agriculture, and cosmetics.[33] The same authors detailed the development of an injectable and self-healing anesthetic oleogel formed through the self-assembly of glycolipids. The glycolipid was prepared by using $\alpha$-chloralose and vinyl ester and self-assembled to form a gel in paraffin oil [Figure 19, (**44**)]. This innovative formulation demonstrated noteworthy anti-biofilm properties and exhibited effectiveness in wound closure within diabetic rats.[125]

To unlock a unique class of smart material, advancements in stimuli-responsive supramolecular gels is a significant challenge. To address this, biobased glycosylfuran amphiphilic gelators were synthesized. These gelators have been employed to construct the hydrogel by *in situ* enolization with encapsulation of NaHS and $H_2S$ [Figure 20, (**45**)].[126] Ohsedo and collaborators synthesized a set of novel compounds incorporating oleoyl, amino acid, and D-glucamine components under mild reaction conditions [Figure 20, (**46**)]. The hydrogelation capacity of these compounds was assessed, which revealed gels with enhanced stiffness and thixotropic properties. The observed performance was contingent upon the chemical structure of the amino acid used and the number of probable hydrogen bonding sites.[127] Two derivatives of gluconic acid,


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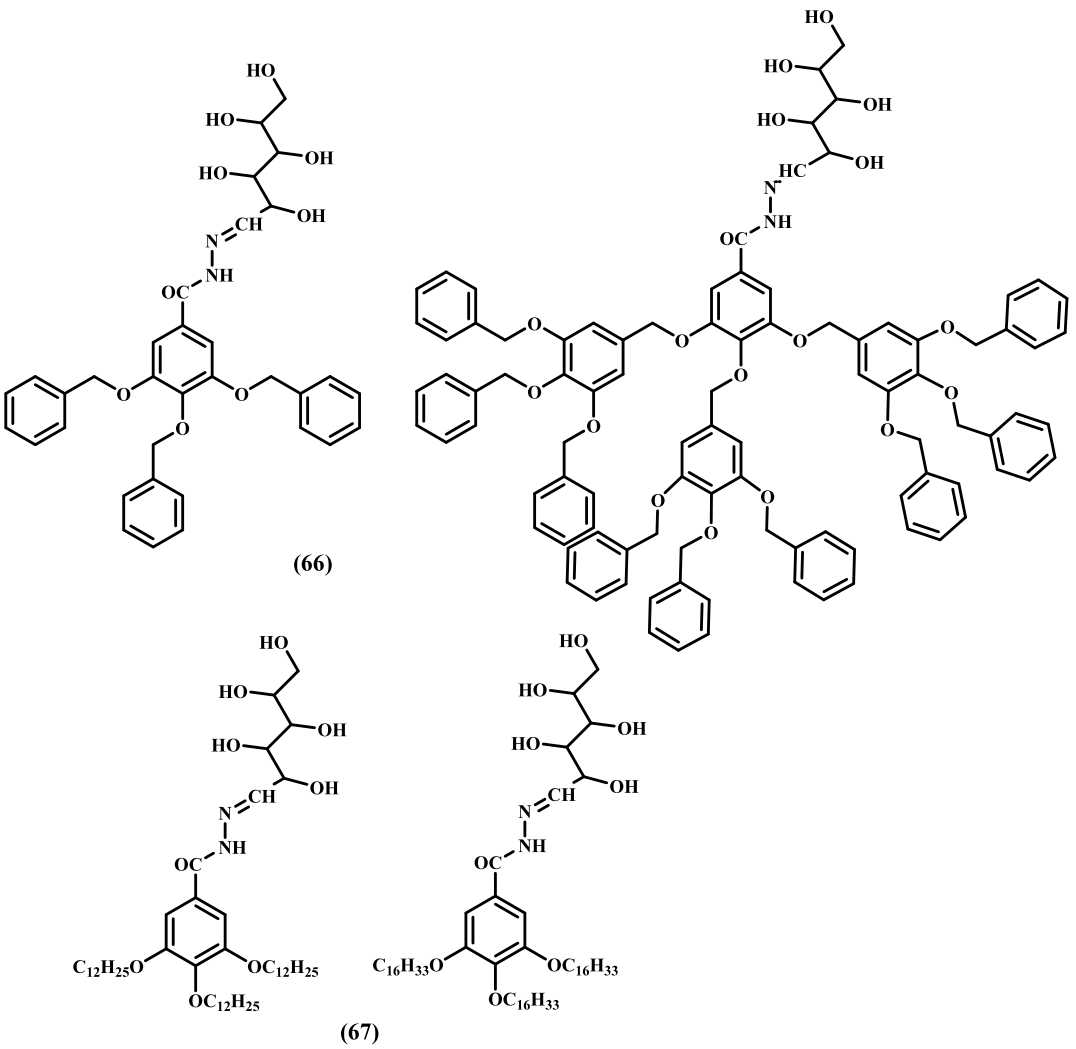


**Figure 27.** Structures representing miscellaneous glycolipid gelators.

namely, C3 and C6, featuring a terpyridyl moiety were conceptualized and synthesized [Figure 20, (**47**)]. Furthermore, the self-assembled structures of these molecules were investigated through a comprehensive approach by employing theoretical calculations. This study provides a robust methodology for the development of smart materials with functional properties.[128]

In recent times, our group has reported the design and synthesis of amphiphilic glycolipids by modulating their structures. The glycolipids were designed using long chain fatty acid as the hydrophobic tail and sugar headgroup as the hydrophilic part connected by aspartic acid as linker. We have varied the chain length, polar headgroup size, and number of unsaturation in the alkyl chain [Figure 21, (**48**) and (**49**)]. This systematic study demonstrated that structural modification in gelator molecules can affect the gelation properties and behavior. These supramolecular gels are further employed to study the encapsulation and release performance of bioactives and in metal removal from vegetable oil.[17,129] Further, one of the gelators from the glycolipids mentioned above was employed to study the *in situ* reduction of gold in its supramolecular gel matrix in the absence of any external reducing/stabilizing agents. This nanocomposite gel, having preferential selectivity toward gold, can also be used as an electrocatalyst material for oxygen reduction reactions.[130]

Roy and co-workers formulated glucose-based gelators with pyridine moieties and alkyl chains. Their gelation ability was checked in a mixture of binary solvents and implemented in absorbing toxic dyes with efficient reusability [Figure 22, (**50**)].[131] In another report, a gluconosemicarbazide gelator displayed gelation ability in the mixture of water and DMSO after heating and ultrasonication. Ultrasound treatment induced gelation at lower concentrations than did thermal treatment. Additionally, the gels transitioned to a solution state at higher temperatures compared with thermally induced gels [Figure 22, (**51**)].[132] The supramolecular gelators on the basis of gluconic acid, amino acids, and hydrophobic alkyl chains were designed. These gelators were able to form a gel in a diverse range of solvents, such as organic solvents, oils, diesels, ionic liquids, and aqueous solutions of all pH ranges. Varying the amino acids displayed the change in the gelation behavior of gelators [Figure 22, (**52**)].[133]

Gelators based on acetals of D-gluconic acid were reported to have stable gelation in extended varieties of ionic liquids at lower concentrations. From this study, it can be inferred that the gelation behavior was significantly affected because of the nature of ionic liquids, alkyl chain length, and hydrogen bonding sites present in gelator molecules [Figure 23, (**53**)].[134] A series of *N*-acetylglucosamine derivatives linked with triazole moieties was prepared and showed excellent gelation in crude oils, diesel,


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*ACS Omega* 2024, 9, 25513−25538

petrol, and organic solvents selectively in the presence of seawater and water. One of the gelators displayed efficient entrapment of synthetic dyes; hence, it was used for selective removal of dye from water [Figure 23, (**54**)].[135] Series of fluorescent gelators containing pyrenyl and glucono groups with diaminoalkane spacers with varying lengths as spacers were formulated [Figure 23, (**55**)]. Correlation among the structures of gelators and respective gels has been analyzed on the basis of the aggregation behavior and Hansen solubility parameters.[136]

**4.5. Glycolipid Gelators Containing Bolaamphiphilic Glycolipids.** Bolaamphiphilic glycolipids are a specific type of glycolipid that consists of two hydrophilic heads connected by a hydrophobic linker. These bolaamphiphilic glycolipids can be designed to self-assemble into well-organized structures in different solvents to form a gel.

The structures of supramolecular hydrogelators featuring bolaamphiphilic glycolipid characteristics demonstrating noteworthy attributes, such as reversible thermochromism and a gel-to-sol transition, were reported.[137,138] The molecular design and synthesis of these hydrogelators incorporated homo- or heterosaccharides at opposing ends [Figure 24, (**56**)] The article deliberates on the impact of saccharide structural variations on gelation proficiency.

The hydrogel-forming ability of biobased glyco-bolaamphiphile [Figure 24, (**57**)] was studied and reported by Baccile and co-workers.[139] The formulated hydrogel displayed a gel-to-sol transition due to the phase change from fibers to micelle. This feature also allowed modification of the elastic properties of glyco-bolaamphiphile hydrogel. Further, the same group reported the bolaamphiphilic sophoroside, a class of bolaform glycolipids composed of sophorose units at both ends obtained by microbial fermentation. Depending upon the conformation of the sophorose group at both ends, it revealed gel-to-sol and micelle-to-fiber transitions [Figure 24, (**58**)].[140] Glyconucleoside bolaamphiphiles with a nitrophenyl group demonstrated gelation in water. These hydrogels were light-sensitive, which led to the photocleavage reaction. The increase in the storage modulus was observed after the photocleavage of nitrophenyl groups. This light-responsive hydrogel could serve as a promising smart biomaterial, thereby allowing on-demand control of gel stiffness for applications in cellular or tissue engineering [Figure 24, (**59**)].[141]

**4.6. Miscellaneous Glycolipid Gelators.** Navigating the diverse landscape of glycolipid gelators, this section unveils the potential of some miscellaneous counterparts by shedding light on their unique structural ideas and multifaceted applications. In this line, a new kind of supramolecular gelator based on glycopeptides was explored extensively. A glycopeptide gelator composed of a D-glucosamine sugar moiety, a tetrapeptide segment, and a naphthyl group was designed to form a hydrogel. This hydrogel was further employed to mimic the glycosylated microenvironment of the extracellular matrix with enhanced cell adhesion properties [Figure 25, (**60**)].[142] In another report, glycopeptide mimetics with modification of the peptide groups at the N-terminal of butylazobenzene was demonstrated. These gelators were self-assembled to give different 1D morphologies with a slight position change of amino acid residue in peptide moieties. Also, the glycopeptide assemblies displayed stimuli-responsive disassembly−assembly behavior to light, temperature, or host−guest chemistry and switchable antibiofilm properties [Figure 25, (**61**)].[143] Glycopeptides based on a naphthalene diphenylalanine carbohydrate conjugate self-assembled to form hydrogels. This supramolecular hydrogel with biocatalytic activity can be used for enzyme prodrug therapy. These enzyme-loaded hydrogels can transform the prodrugs into anticancer drugs and can be employed as injectable biocatalytic reactors [Figure 25, (**62**)].[144]

LMWGs based on tris-urea with hydrophilic glucosides arranged onto the circle of the hydrophobic part were introduced. The formed hydrogel demonstrated the gel-to-sol transition in response to lectin and anion. Hence, this hydrogel can have future applications in the area of chemical sensors [Figure 26, (**63**)].[145] Das and co-workers reported the facile and regioselective synthesis of bis-triazologlycolipids recognized as organogelators by click reaction [Figure 26, (**64**)]. Subsequent scrutiny of the gelators' morphology and self-assembly characteristics was thoroughly studied via FE-SEM and high-resolution TEM (HR-TEM) analyses.[146] New glycolipid series containing diacetylene groups with structural modifications were reported. Their self-assembling properties were studied, and it was observed that the chain length and diyne position have a prominent impact {Figure 26, (**65**)].[147] The same group further modified these diacetylene containing glycolipids with urea and amide derivatives with D-glucosamine. They have shown good gelation abilities and produced light-responsive diacetylene gels, which cross-linked to give blue/purple gels under UV light of 6 W.[148]

Prasad and co-workers reported poly(aryl ether) dendron-based gelators containing glucose to form hydrogels. These hydrogels demonstrated an *in situ* reversible transition from nanofibers to spherical aggregates in response to pH change. Graphene oxide dispersion resulted in lowering the gelation concentration and increased the mechanical strength of the gel to produce an efficient hybrid gel [Figure 27, (**66**)].[149] These glucose-based gelators were modified with a long alkyl chain in their structure and screened for gelation behavior and other properties. It was observed that the dendron-based gelators can act as effective drug carriers and can be explored in drug delivery systems [Figure 27, (**67**)].[150]

## 5. CHARACTERIZATIONS

Supramolecular gels represent an intriguing category of soft materials characterized by dynamic and reversible noncovalent interactions that govern the formation of a 3D network. This inherent dynamism imparts a unique responsiveness to external stimuli, thereby making thorough characterization essential for a detailed understanding of these materials. However, the diverse and dynamic nature of supramolecular gels poses challenges for their characterization. Therefore, a crucial aspect of research involves employing various techniques, including NMR spectroscopy, computational methods, X-ray diffraction, microscopy (SEM, FE-SEM, HR-TEM), rheology, dynamic light scattering, and thermal analysis.[37,151,152]

Nuclear magnetic resonance (NMR) spectroscopy stands out as a powerful tool by providing detailed information about the molecular interactions in the overall gel network. Computational techniques with experimental methods offer predictive models to elucidate complex gelation processes. X-ray diffraction techniques enable the investigation of spatial arrangement of molecules within the gel structure, thereby shedding light on the supramolecular organization. Microscopy techniques, including scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM), offer high-resolution imaging and provide visualization of the gel morphology and understanding of the gelation mechanism at the microscopic level.


https://doi.org/10.1021/acsomega.4c00958
ACS Omega 2024, 9, 25513−25538

**Table 1. Applications of Glycolipid-Based Supramolecular Gels**

| gelator | applications/studies | reference |
|---|---|---|
| glycolipid gelators based on renewable sources | | |
| **1** | in hydrophobic drug delivery systems | Vemula et al. [72] |
| **2** | gelation behavior, self-assembly, and properties | John et al. [61, 73, 74] |
| **3** | gelation behavior, self-assembly, and properties | Jung et al. [48] |
| **4** | self-assembly, chemical selectivity toward guest binding | John et al. [76] |
| **5** | gelation behavior, self-assembly, and properties | Lalitha et al. [77] |
| **6** | in disrupting the bacterial biofilms | Prasad et al. [68] |
| **7** | biofilm inhibition and antimicrobial activity | Prasad et al. [67] |
| **8** | in situ synthesis and stabilization of gold nanoparticles | Vemula et al. [78] |
| **9** | antioxidant, foaming, and emulsifying properties | Nandi et al. [79] |
| **10** | gelation behavior, self-assembly, and properties | Carretti et al. [45] |
| **11** | pH dependent morphology transitions | Cuvier et al. [80] |
| **12** | gelation behavior, self-assembly, and properties | Messaoud et al. [52] |
| **13** | gelation behavior, self-assembly, and properties | Baccile et al. [81] |
| **14** | in heavy metal removal and metallogel and hybrid gel formation | Poirier et al. [54, 82−84] |
| **15** | gelation behavior, self-assembly, and properties | Gao et al. [85] |
| **16** | hybrid nanomaterial synthesis and catalytic applications | Saha et al. [86] |
| **17** | gelation behavior, self-assembly, and properties | Imura et al. [91] |
| glycolipid gelators based on monosaccharides | | |
| **18** | gelation behavior, self-assembly, and properties | Jung et al. [94] |
| **19** | formulation of fluoride-responsive gels | Tsai et al. [95] |
| **20** | gelation behavior, self-assembly, and properties | Mathiselvam et al. [96] |
| **21** | gelation behavior, self-assembly, and properties | Cui et al. [97] |
| **22** | gelation behavior, self-assembly, and properties | Soundarajan et al. [98] |
| **23** | gelation behavior, self-assembly, and properties | Soundarajan et al. [99] |
| **24** | phase-selective gelators for marine oil spill recovery and removal of dye from polluted water | Soundarajan et al. [100] |
| **25** | Dye removal and photoresponsive and phase-selective gelation | Jenifer et al. [101] |
| **26** | encapsulation and release of drugs | Morris et al. [102] |
| **27** | entrapment and release of naproxen sodium | Chen et al. [103] |
| **28** | gelation behavior, self-assembly, and water-sensitive properties | Ludwig et al. [107] |
| **29** | gelation behavior, properties, and crystal formation | Cui et al. [108] |
| **30** | gelation behavior, properties, and salt-dependent morphology change | Li et al. [109] |
| **31** | selective dye adsorption, hybrid gel and bead formations, metal reduction, and catalysis | Okesola et al. [110], Albino et al. [13], Piras et al. [111, 112] |
| glycolipid gelators based on disaccharides | | |
| **32** | gelation behavior, self-assembly, and properties | Bhattacharya et al. [113] |
| **33** | enzyme induced gel-to-sol transition | Akama et al. [115] |
| **34** | as a sensor for cholera toxin | Biswakarma et al. [116] |
| glycolipid gelators based on disaccharides | | |
| **35** | gelation behavior, self-assembly, and liquid crystalline properties | Clemente et al. [117] |
| **36** | photoresponsive gel-to-sol transition and thermal *cis*−*trans* isomerization | Clemente et al. [118] |
| **37** | gelation behavior, self-assembly, and liquid crystalline properties | Clemente et al. [119] |
| **38** | photoresponsive and liquid crystalline properties | Clemente et al. [120] |
| **39** | peanut agglutinin (PNA) lectin binding ability | Cano et al. [121] |
| **40** | gelation behavior, self-assembly, and properties | John et al. [122] |
| **41** | gelation behavior, self-assembly, and properties | Hibert et al. [123] |
| glycolipid gelators based on derivatized sugar | | |
| **42** | development of trimethylamine sensor fabric | Thamizhanban et al. [124] |
| **43** | gelation behavior, self-assembly, and properties | Thamizhanban et al. [33] |
| **44** | antibiofilm, anesthetic and diabetic wound skin repair properties | Prasad et al. [125] |
| **45** | pH-responsive and in situ enolization with encapsulating NaHS and $H_2S$ | Thamizhanban et al. [126] |
| **46** | gelation behavior, self-assembly, and properties | Ohsedo et al. [127] |
| **47** | thermo- and chemical stimuli response in luminescence | Zhang et al. [128] |
| **48** | bioactive encapsulation and enzymatic release | Holey et al. [17] |
| **49** | bioactive encapsulation and release, metal removal | Sekhar et al. [129] |
| **50** | toxic dye removal and oil spill recovery | Khan et al. [131] |
| **51** | ultrasound and temperature-induced gelation | Himabindu et al. [132] |
| **52** | gelation behavior, self-assembly, and properties | Minakuchi et al. [133] |
| **53** | gelation behavior, self-assembly, and properties | Chen et al. [134] |
| **54** | phase-selective gelation and selective dye removal | Narayana et al. [135] |
| **55** | gelation behavior, self-assembly, and properties | Yan et al. [136] |
| glycolipid gelators containing bolaamphiphilic glycolipids | | |
| **56** | gel−sol transition with reversible thermochromism | Oosumi et al. [137], Tsutsumi et al. [138] |
| **57** | gel-to-sol morphological transition | Baccile et al. [139] |
| **58** | gel-to-sol morphological transition | Poirier et al. [140] |
| **59** | light-responsive photocleavage reaction | Bansode et al. [141] |
| miscellaneous glycolipid gelators | | |
| **60** | in tissue engineering and as a biomimetic scaffold for vascularization | Qi et al. [142] |
| **61** | switchable antibiofilm properties and stimuli responsiveness | Chen et al. [143] |
| **62** | as therapeutic reactors for enzyme prodrug therapy | Sakamoto et al. [144] |
| **63** | responsive toward lectin and anion | Yamanaka et al. [145] |
| **64** | gelation behavior, self-assembly, and properties | Hemamalini et al. [146] |
| **65** | gelation behavior, self-assembly, and properties | Nie et al. [147] |
| **66** | pH-dependent transition and hybrid gel formation | Rajamalli et al. [149] |
| **67** | entrapment and release of drugs | Kannan et al. [150] |



https://doi.org/10.1021/acsomega.4c00958
*ACS Omega* 2024, 9, 25513−25538

Dynamic light scattering (DLS) provides insights into the size distribution of gel particles and their dynamic behavior, while thermal analysis methods, such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), offer information on the thermal stability and phase transitions of supramolecular gels. Rheological studies play a vital role in characterizing the mechanical properties of supramolecular gels by providing information about their viscoelastic behavior and structural stability. By carefully selecting and combining these characterization techniques, researchers can develop a comprehensive understanding of the complex intermolecular forces, gelation mechanisms, and influencing factors that define the properties of supramolecular gels.

Overall, the characterization of supramolecular gels is a multidisciplinary endeavor that combines experimental and computational approaches to unravel the complexity of these materials. Given the diverse gelation mechanisms and influential factors governing supramolecular gels, careful selection and application of characterization methods are paramount to harnessing their respective advantages effectively and advance a better investigation of these materials.

## 6. APPLICATIONS

Nature offers abundant opportunities for the synthesis of amphiphilic molecules derived from renewable sources, thereby showcasing multifunctional applications.[26,68] Glycolipid amphiphiles featuring a hydrophilic sugar headgroup with a hydrophobic part exhibit gelation properties.[119,133,153] The mechanical stability and gelation properties of glycolipid gelators are strongly influenced by their molecular structure in various solvents.[63,119] Consequently, a systematic exploration of the gelation study of amphiphiles is essential for the strategic design of glycolipids and their applications. The studies and application of glycolipid-based supramolecular gels cited in this review are demonstrated in Table 1.

Glycolipid-derived supramolecular gels find diverse applications in soft optical devices, $CO_2$ absorption, lectin binding, oil spill recovery, and the sequestration of alkali metal ions.[7,154] These amphiphilic organo/hydrogels possess the capability to encapsulate hydrophilic/hydrophobic drugs within their self-assembled 3D networks, thereby enabling controlled release of bioactives.[31,155] Hydrogels and gel emulsions exhibit versatile applications in the preparation of food gels by demonstrating several characteristics.[156,157] The release behavior of bioactives from these gels is contingent on the response of supramolecular self-assembled structures to external stimuli, including temperature, light, electric fields, enzymes, and pH.[142] Furthermore, the supramolecular self-assembly of amphiphiles serves as binding sites for metals and dyes, thereby demonstrating an ability to bind and remove dyes and metal ions.[158] Consequently, the guest-binding and porous nature of amphiphilic self-assembled structures holds promise for probable applications in water purification.[100,159] In addition to their role in water purification, gels exhibit extensive biomedical and sensory applications, which solidifies their status as versatile materials.[160−162] This multifaceted nature positions gels as powerful tools with significant potential in various scientific and technological domains.[163−166]

## 7. CONCLUSION AND PERSPECTIVE

Glycolipid-based gelators represent a rapidly developing area of research with a vast potential across various fields. Their unique properties and diverse functionalities offer exciting opportunities for the development of novel soft materials. This review provides a summary of recent advancements in the design, synthesis, and applications of glycolipid-based gelators with a specific focus on their self-assembly mechanisms. Amphiphilic glycolipid molecules, easily synthesized with the incorporation of diverse functional groups, are emphasized for their gelation behavior and self-assembling properties. A thorough exploration of the impact of structural variations of glycolipid gelators on gelation behavior and properties is undertaken. It concludes with a presentation of selected applications of these supramolecular gels sourced from the literature and underscores their significance. The review not only highlights current trends but also showcases recent advances in supramolecular gels employing amphiphilic glycolipid-based LMWGs. The potential of implementing supramolecular gels derived from glycolipids is important in the context of numerous technological applications anticipated in the future. The overarching goal of this review is to shed light on the fundamental design principles and key structural features that hold relevance for glycolipid-based gelators. By doing so, we aspire to provide valuable guidelines for researchers operating at the interdisciplinary intersection of chemistry, biochemistry, and materials science.

Future research will focus on further exploring the design principles of glycolipid gelators and tailoring their properties for specific applications at a deeper molecular level. Despite significant advancements in the field of supramolecular gelation during the past decades, the exact mechanism behind complex gelation is still less known. Additionally, investigating the biocompatibility and biodegradability of glycolipid-based gels could pave the way for their application in various biomedical fields, such as drug delivery, tissue engineering, and regenerative medicine. Exploring the potential synergy between glycolipid-based gelators and other materials could lead to the development of multifunctional hybrid materials with tailored properties for specific applications. Overall, by addressing these future perspectives, glycolipid-based gelators hold immense potential to contribute to diverse fields.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

S.A.H. gratefully acknowledges Department of Science and Technology (DST), New Delhi for providing INSPIRE fellowship. The authors acknowledge Director, CSIR-IICT (Manuscript Communication Number: IICT/Pubs./2024/



https://doi.org/10.1021/acsomega.4c00958
ACS Omega 2024, 9, 25513−25538

034) for providing all the necessary facilities to carry out the work.

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https://doi.org/10.1021/acsomega.4c00958
*ACS Omega* 2024, 9, 25513−25538