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MINI REVIEW

Applications of Supramolecular Materials in Real World: A Mini Review

ANSHUPRIYA SHOME

Department of Chemistry, Brahmananda Keshab Chandra College, 111/2, Barrackpore Trunk Rd, Dunlop, Saket Nagar, Bonhooghly, Kolkata, West Bengal, Kolkata-700108, India

Corresponding author: E-mail: ashome9@gmail.com

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The breakthrough in supramolecular chemistry came in the 1960s when Charles J. Pedersen utilized the concept of 'chemistry beyond molecules' in the synthesis of the crown ethers. Self-assembly could allow for the construction of fascinating supramolecular architectures that are otherwise challenging to prepare using covalent chemistry. Supramolecular chemistry has been extensively studied in recent decades and its applications have been explored to include everything from molecular machines and sensors to gas absorption and nanoreactors to chemical catalysis and drug delivery. In this review article, some of the commercial applications are discussed to highlight the transition of supramolecular chemistry from theoretical concept to market.

Keywords: Supramolecular chemistry, Molecular assemblies, Self-healing, Cyclodextrin, Polyrotaxanes, Supramolecular medicine.

INTRODUCTION

It is nature's ability to create order out of disorder that makes it so beautiful. The atoms, planets, stars and even galaxies are originated from self-organization of fundamental particles produced from Big-Bang. Again, a closer look to the living systems reveals that from basic unit of life, 'cell' to complex multicellular organism is the beautiful manifestation of self-assembly. The continuous effort to understand the secrets of nature leads to the development of a new interdisciplinary area of science 'supramolecular chemistry'. Non-covalent intermolecular forces, such as hydrogen bonding, π–π stacking, donor-acceptor contacts, metal coordination, solvophobic forces and van der Waals interactions, bring together two or more chemical species to form supramolecules. Thus, supramolecular chemistry is "the chemistry of molecular assemblies and intermolecular bonds [1-6]. In self-assemblies, the variations in the size, shape and geometric complementary of constituent molecules provide them amazing features, which are more than the sum of its parts. Supramolecular aggregation is successful when a right balance between attractive forces and Brownian motion is achieved. The formation of the unique structure is always a reversible process *i.e.*, self-assembled structures are dynamic in nature [7]. The components are continuously forming supramolecules and again breaking apart under strict equilibrium, still giving extremely robust structures from soft matter under a given set of conditions. So self-assembly is a parallel process, which is controllable. Self-assembled structures are self-correcting, which means that if molecules in an aggregate are arranged erroneously, Brownian motion will shuffle them and they will have a new opportunity to rearrange themselves properly. Moreover, they are self-healing. If they are broken as a result of external shock but can be repaired [8].

The importance of supramolecular chemistry was recognized when Nobel Prize for Chemistry in 1987 was awarded to D.J. Cram, J.-M. Lehn and C.J. Pedersen for their work in this area [9]. With time researches in this area have gained a rapid pace and various supramolecular systems with real life applications have been developed. In 2016, Nobel Prize for Chemistry was achieved by J.-P. Sauvage, Sir J.F. Stoddart and B.L. Feringa for the design and production of molecular machines [10]. Nowadays industries are utilizing this field of chemistry into next generation technologies for the development of everyday commercial and marketable products [11,12]. In fact, micelles of surfactant molecules were utilized for cleaning long before the term 'supramolecular chemistry' was coined. Knowledge

of supramolecular chemistry has allowed to take advantage of its remarkable properties in a wide variety of contexts, including commonplace objects, sensors, drug delivery vehicles, regenerative treatments, metal extraction methods, *etc.* [11-17].

Supramolecular chemistry in medicines: Supramolecular medicine is a branch of medicine that focuses on the use of molecular assembly to improve medical treatment and are utilized for the diagnosis, treatment and prevention of disease. Because of their unique characteristics, these materials have attracted a lot of attention from scientists and medical professionals working in drug delivery, disease diagnostics and imaging and regenerative medicine [18]. Despite much progress in research, the lack of clinical approval of nanomedicines limits its real-life applications to some extent.

Liposomal drug delivery: Liposome is a kind of self-assembly, which has a closest resemblance with the cell membrane. Reduction in the non-specific side-effects and the toxicity of encapsulated drugs can be achieved by using target specific liposomes [19]. As a drug delivery system, liposomes have several advantages like biocompatibility, power of self-assembly, ability to carry large drug loading and supramolecular characteristics that can be modified to control their effects on biological systems. Traditional liposomes, sterically stabilized liposomes, and ligand-targeted liposomes are the three most common forms of liposomal delivery vehicles [19-23].

Conventional liposomes are composed of aqueous compartments enclosed by lipid bilayer membrane of twin chain phospholipid surfactants having cationic, anionic or neutral phospholipids and cholesterol, with both polar ends facing the aqueous medium. The formation of liposome is thermodynamically stabilized by hydrogen bonding, van der Waals forces and other electrostatic interactions. Liposomes are able to contain both hydrophilic and hydrophobic compounds due to their aqueous core and lipid bilayer (Fig. 1). Improved solubility and stability of the encapsulated drugs have made liposome an excellent vector for drug delivery. The drug can avoid early degradation, inactivation and dilution in circulation [23]. Most importantly liposomal formulations reduced the toxicity of drugs *in vivo*, through modifying absorption, distribution, metabolism and excretion (ADME) mechanism of drugs in comparison to free drug. But the main challenge in the clinical applications of liposome is confrontation with body defense system. When liposome like any other foreign particle enters the body, it encounters multiple defense systems which recognize, neutralize and eliminate invading substances. These defenses majorly include reticuloendothelial system (RES) [23-25]. After being administered, liposomes tend to collect in the liver, spleen, kidney, lungs, bone marrow and lymph nodes, all of which are connected with the RES and where they eventually become ineffective. Liposomes are removed from the blood by phagocytic cells in the RES through the interactions between those cells and the liposomes. The opsonization process of labeling foreign pathogens for removal by phagocytes slows down with a decrease in liposome size from 800 to 200 nm [23]. So, liposomal formulation should be designed in such a way that it can escape the RES, *i.e.* body's innate immune system and reach to target organ and release drugs there. The strategy

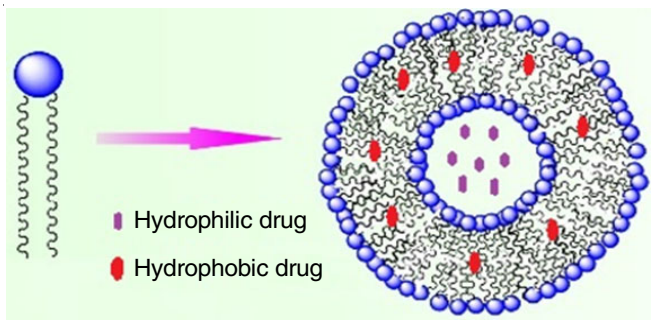

Fig. 1. Structure of liposome

is the conjugation of PEG polymers to the liposomal membrane for improved circulation times and avoiding removal by the RES through stealth mechanism. PEGylation creates a highly hydrated surface, which inhibits both electrostatic and hydrophobic interactions with plasma. So, there is no doubt that stealth liposomes *i.e.* PEGylated liposomes are at the focus of liposomal drug delivery. Liposomal stability can be improved and phospholipid exchange with other circulating structures reduced through cholesterol inclusion, *e.g.*, red blood cells and lipoproteins. Integrating cholesterol into small electrostatically neutral liposomes with size nearly 100 nm, can increase the circulation time up to several hours. Additional improvement of liposomal delivery systems is achieved by active targeting and triggered release [26].

Activated targeting involves the attachment of target-specific ligands to the outer membrane of liposomes for use in a range of biomedical applications. Henceforth, the supramolecular chemistry has been widely investigated experimentally both *in vitro* and *in vivo* [27-34]. Targeting ligands can enhance the specificity of encapsulated drug delivery to diseased tissues and cells, without affecting the non-target sites. In this context, folate attached liposomes have shown improved biodistribution of liposomes in folate-expressing tumors in a murine model [35]. In a rodent model of musculoskeletal pain, the efficacy of loperamide-encapsulated liposomes was improved by binding ICAM-1 monoclonal antibodies to their surface [36]. Doxorubicin-loaded anti-HER2 immunoliposomes have also shown improved therapeutic efficacy in comparison to free doxorubicin or nontargeted liposomal doxorubicin [37].

Many liposomal products are on the market (Table-1) and many drugs are still undergoing clinical trials to test their toxicity and therapeutic efficacy [19]. PEGylated liposomes are used to provide doxorubicin, a nano-drug that has been approved by FDA. PEGylated liposomal doxorubicin (PLD) is used in the treatment of a wide range of cancers when combined with other medications. This includes AIDS-related Kaposi's sarcoma, leukaemia and cancers of the ovary, breast, bone, lung and brain. Since, PLD reduces the amount of free drugs in the bloodstream resulting in the reduction of the cardiotoxicity. More liposomal-based medicines are being tested for the medicinal efficacy and biodistributions in human clinical trials. Problems with pharmaceutical production, regulatory restrictions and intellectual property have slowed the practical implementation of liposomal drug delivery despite a large body of good research data obtained over the past 50 years (IP).

TABLE-1
MARKETED LIPOSOMAL-BASED THERAPEUTICS AND PRODUCTS IN CLINICAL DEVELOPMENT

Drug	Disease	Status	Type of liposomal-based delivery systems
Verteporfin	Molecular degeneration	FDA Approved in 2000	Cationic
Vincristine l	Non-Hodgkin lymphoma	FDA Approved in 2012	Conventional
Amphotericin B	Anti-fungal prophylaxis	FDA approved in 1997	Conventional
Daunorubicin	Leukemia and solid tumors	FDA Approved in 1996	Conventional
Cytarabine or cytosine arabinoside	Neoplastic meningitis and lymphomatous meningitis	FDA Approved	Conventional
Morphine sulfate	Pain Management	FDA Approved in 2004	Conventional
Doxorubicin	Leukemia, breast cancer, bone cancer, lung cancer, brain cancer	FDA Approved in 1995	PEGylated
Doxorubicin and bortezomib	Relapsed or refractory multiple myeloma	FDA Approved in 2007	PEGylated

Cyclodextrins in drug delivery: Cyclodextrins (CDs) are basically the cyclic oligosaccharides made up of glucose monomers linked by α-1,4-glycosidic bonds. There are majorly three classes of cyclodextrins, α, β and γ-CDs (Fig. 2) are formed from 6, 7 and 8 D-glucose units, respectively [38-40].

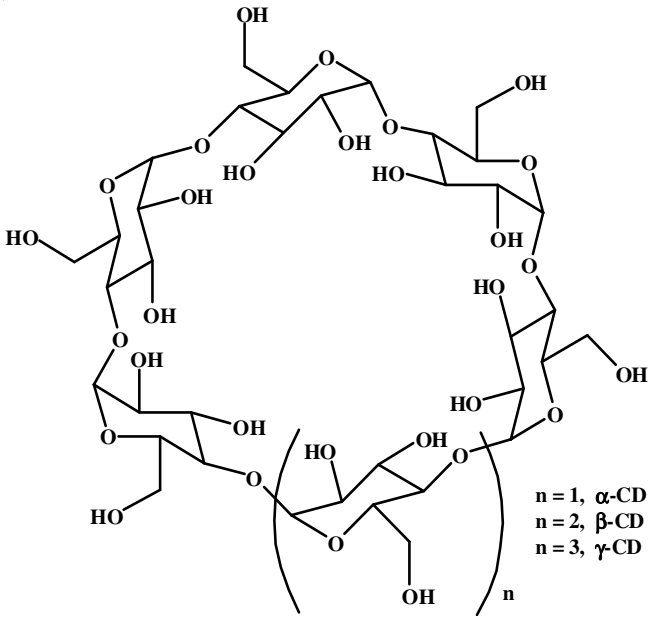

Fig. 2. Chemical structure of α, β and γ-cyclodextrins

Due to their unique doughnut shape and hydrophobic cavity (Fig. 2), cyclodextrins are able to encapsulate tiny hydrophobic molecules or moieties within their hydrophilic outer surface. The major advantages of the natural cyclodextrins as delivery vehicles are (1) definite chemical structure with potential sites for target specific modification or conjugation; (2) easy modulations of cavity size; (3) biocompatibility; (4) water solubility; (5) protection of encapsulated drugs and (6) low cost of synthesis and ease of purification [41]. For decades, they have been applied in pharmaceuticals, drug delivery systems, cosmetics, food and chemical industries [41-48]. Commercially, several cyclodextrin-based oral formulations are available. When administered orally, cyclodextrins should serve only as a delivery vehicle, helping to bring the medication from its original aqueous environment to the mucosal surface of gastrointestinal tract for lipophilic absorption. Digoxin is a drug which is used to treat heart failure, but susceptible to acidic hydrolysis. The acid-catalyzed hydrolysis of digoxin is slowed down by cyclodextrins. γ-Cyclodextrin complex can improve the oral absorption of digoxin by decreasing acid hydrolysis of drug [49]. As a result, digoxin is mixed with γ-cyclodextrin to form a water soluble formulation for oral tablet use and to avoid acid degradation of the drug by gastric juices [50]. The oral steroid complexes with cyclodextrins are also effective when taken orally [51-56].

In addition to oral administration, cyclodextrin can also be used as an ocular drug delivery vehicle. The benefits of cyclodextrins in the ophthalmic use include enhanced medication solubility and stability, as well as reduced irritation and discomfort. An ophthalmic drug delivery vehicle must not irritate the ocular surface since irritation causes rapid washing of the inculcated drug. Since their hydrophilic outer layer makes them harmless for use in an aqueous eye drop, hydrophilic cyclodextrins have become an excellent choice for this application. However, cyclodextrins increase the ocular concentration of hydrophobic medicines despite their inability to cross biological barriers like cornea [57-60]. One example is, an ocular delivery system (eye drops) based on complex of dexamethasone (Fig. 3) and γ-CD nanoparticles are developed by Oculiss Company. The combination of 1.5% dexamethasone and γ-CD nanoparticles showed promise in reducing central macular thickness (CMT) and improving visual acuity in patients with diabetic macular oedema (DMO). This formulation is also effective in the treatment of painful ocular congestion without any incidence of reoccurrence [60]. Moreover, several anticancer CDs-based drugs are subjected to clinical evaluation [61]. Cyclodextrin can also be used for the delivery of the gene-therapeutic agents such as plasmids, viral vectors and antisense constructs [62].

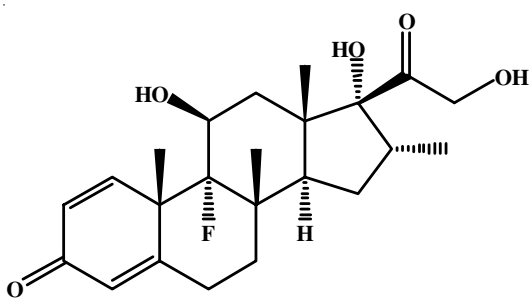

Fig. 3. Structure of dexamethasone

Supramolecular sensor: Supramolecular systems are emerging as an ideal candidate for chemo-sensing due to their special characteristic features. Supramolecules can form highly ordered and complex systems without any covalent bond formation, so sensor development would be easier and rapid [63,64]. Supramolecular systems are highly adaptive in nature due to weak intermolecular interactions present in supramolecular assemblies. They can change their configurations in response to various external stimuli like pH, temperature, pressure, presence of specific chemical, *etc*. These stimuli responsive supramolecular assemblies are highly reversible in nature *i.e.* once the external stimulus is removed, the supramolecular host can reorganize itself to its original state [65]. This reversibility has made supramolecular sensors superior over single-use sensors that rely on covalent bond formation. Introduction of the target analyte can cause a measurable change in a detectable signal including changes in colour [66-68], changes in the Raman spectral signal [69,70], changes in the mass of sensor [71-73] or analytical property [74] after a target analyte binds. In this regard, luminescent sensors depend on sensor-analyte, sensor-fluorophore and fluorophore-analyte interactions [75-77].

In 1990s, DeSilva *et al*. [78] utilized the concepts of host–guest chemistry and fluorescence in the field of optical sensing to quantify sodium ion level within blood serum. This technology is now promoted for use in critical care units in hospitals, ambulances and even veterinary settings [79,80]. Several important bioprocesses, including ion transport, pH regulation, and nerve signal transmission, are controlled by the Na^+ concentration near membranes [81]. So, excellent sensor is required, which can accurately measure local Na^+ levels near model membranes as well as shows excellent selectivity against H^+ [82]. Izatt *et al*. [83] have attached a crown ether to a fluorophore system capable of photoinduced electron transfer (PET) (Fig. 4). The benzo-15-crown receptor has well-known binding affinity towards Na^+. As a crucial point, the performance of the receptor is not impacted by changes in pH since it lacks a pH-sensitive unit. Because of its high hydrophobicity, anthracene was employed as a fluorophore in the receptor, as it is easily taken up by the micellar membrane [84]. When R is an electron-withdrawing substituent, anthracene participates in a non-radiative PET process in the absence of Na^+ [85]. However, the PET quenching is disrupted when sodium is present because the crown ether encloses the sodium, removing electron density from the aromatic ring linked to crown [78]. As a result, fluorescence would be 'turned on', allowing the concentration of sodium in sample to be determined by measuring the resulting increase in luminescence. Calcium and potassium, among others, can also be extracted using this procedure [79,80,86,87].

Another example of supramolecular sensing is glucose sensor. To prevent hypo- and hyper-glycemia, continuous glucose monitoring is essential for all hospitalized patients, especially those with diabetes and those in the intensive care unit (ICU) [88-90]. So much research has been done to develop efficient D-glucose sensors. High performance was found in sensors made from boronic acid derivatives and sugars that interact with each other through hydrogen bonding and

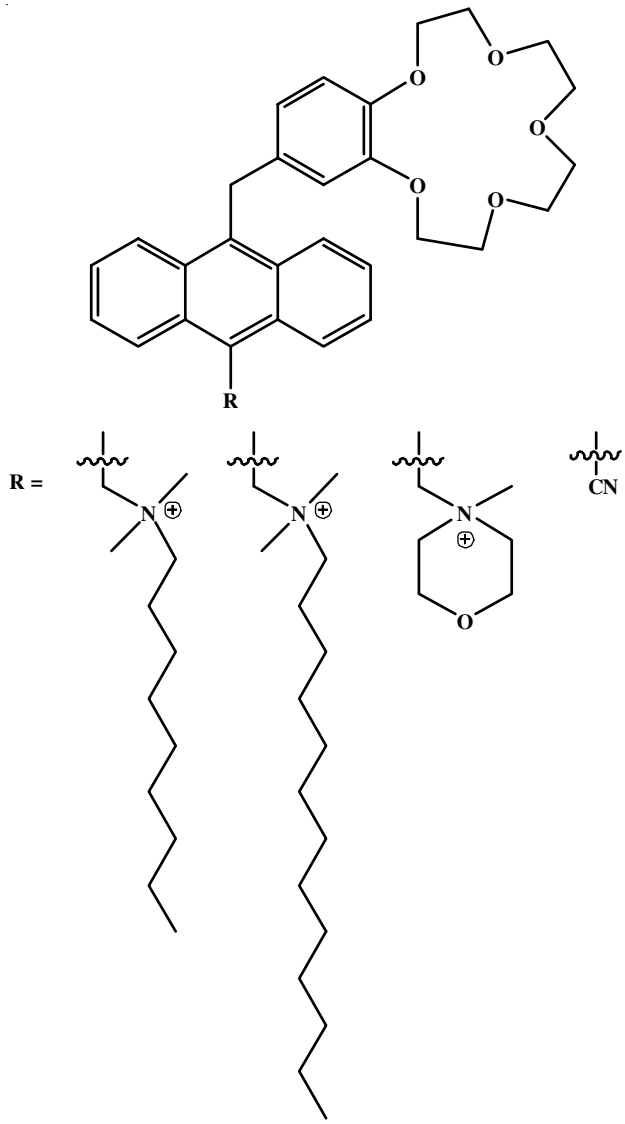

Fig. 4. Structures of various fluorescent sodium sensors

ester formation [91-95]. In early 2015, James *et al*. [96] developed successfully another sensor based on supramolecular interactions. In this sensor, at physiological pH, a phenylboronic acid bearing an amino methyl group in the *ortho*-position binds saccharides (Fig. 5).

A free lone pair of electron on the amino group is responsible to cause PET quenching when the system was coupled to a fluorophore. However, the PET would be disrupted and fluorescence would be 'turned on' when the boronic acid bound saccharide *via* the lone pair on amine. D-glucose concentration is directly correlated with the amount of fluorescence which may be observed. Two companies *viz*. Eversense and Glysure Ltd., use these innovations by preparing and marketing the fluorescent *o*-aminomethyl phenylboronic acids [96-98]. This technique has shown a huge improvement in the accuracy of blood glucose monitoring. The sensor is immobilized within a hydrogel, copolymerized with a fluorescent indicator [96]. The immbilized hydrogel in glysure sensor is filled with optical fibre surrounded by a dialysis membrane. The microporous membrane inhibits blood cells from entering the sensor. The

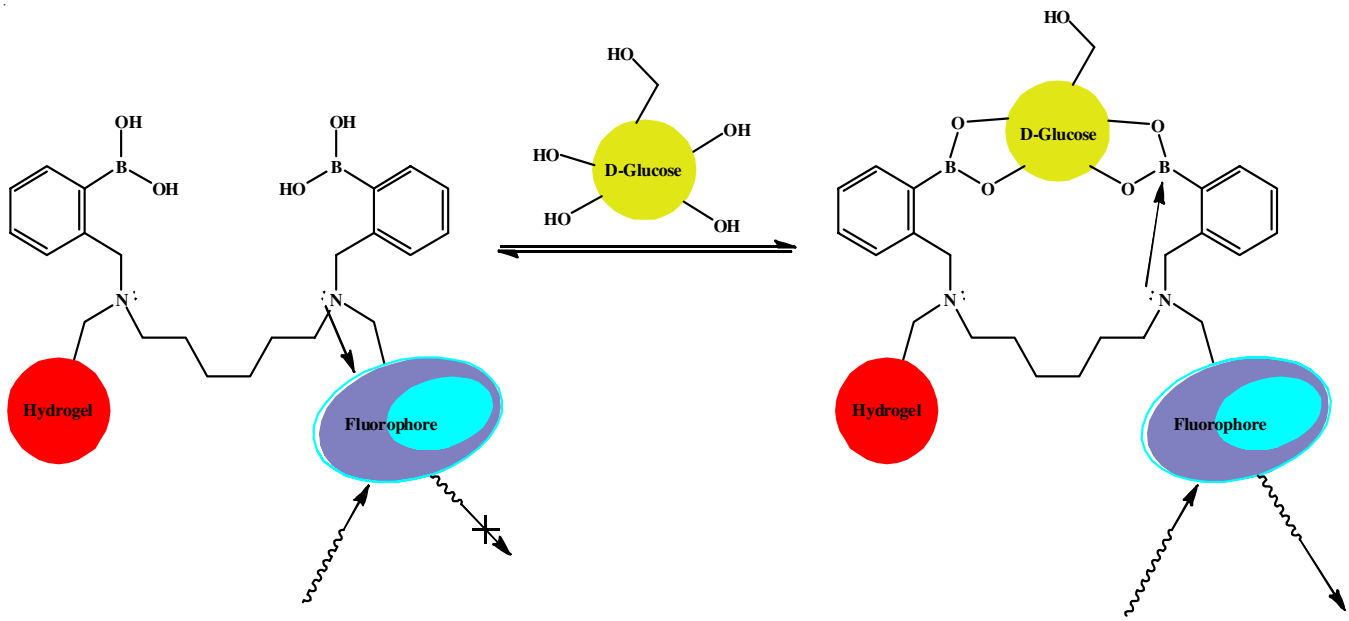

Fig. 5. Chemical structure and proposed glucose binding mode

subcutaneous Eversense sensor is incorporated in a rigid and biocompatible polymer capsule and quantify glucose concentration in interstitial fluids. Externally worn device connected with the inserted sensor records the information. This new method is continuous, making it advantageous over conventional intermittent examination of glucose levels. Both companies have received CE Mark approval in 2015 (Glysure) and 2017 (Eversense) [16].

Supramolecular assembly for regenerative medicine: Regenerative medicine can repair tissue or organs damaged by disease, trauma or congenital defects. Tissue engineering, cellular therapy, medicinal devices and artificial organs are among the technologies employed to achieve this goal. Materials that can mimic the native extracellular matrix (ECM) of tissues play an important role in regenerative medicine strategies. The ECM provides a proper environment to the embedded cells for their survival and growth. The supramolecular biomaterials can be used in development of ECM due to their ability to adapt the cell behaviour because of dynamic non-covalent interactions. Supramolecular adhesive hydrogels are now emerging field of research due to their ability of repairing tissue in various organs like primarily dermal tissue, muscle tissue, bone tissue, neural tissue, vascular tissue, oral tissue, corneal tissue, cardiac tissue, fetal membrane, hepatic tissue and gastric tissue [99]. To serve the purpose supramolecular hydrogels should be biocompatible enough and should not produce any cytotoxic side products upon degradation [100]. Supramolecular polymers of biological relevance are also researched for their potential applications in tissue engineering and regenerative medicine [101-106].

The extracellular matrix (ECM) must fulfil a number of requirements for 3D cell growth, such as providing conditions similar to those the cells would experience *in vivo*, such as the hydrogel matrix. Adhesion sites for cells must be incorporated into the hydrogel. Moreover, the hydrogel should be capable of capturing, stabilizing and releasing tissue-specific growth factors [101]. For example, the RGD or RGDS peptide sequence attached to the supramolecular materials like self-assembled monolayers [107-111], small molecule hydrogelators [112-115], vesicle-forming block copolymers [116,117] and supramolecular polymers [118] can make them bioactive. These supramolecular materials could provide ideal environment for adhesion and growth of fibroblasts [119], breast cancer cells [120] bone marrow mononuclear cells (BMNCs) [121] and rat-derived mesenchymal stem cells (rMSCs) [122] *in vitro* and can be utilized for the development of regenerative medicine [119-124]. Furthermore, RGDS-Peptide amphiphile, a tissue that does not regenerate naturally, can promote the production of tooth enamel [125,126]. In 2013, peptide P11-4 (Ac-QQRFE-WEFEQQ-NH2), commercially known as Curodontt, was applied to repair early dental lesions in patients resulting in the remineralization within 30 days of treatment [127]. The peptide P11-4 can self-assemble into β-sheets with fibrous architectures through electrostatic interactions between arginine and glutamic acid, hydrophobic interactions between aromatic rings and hydrogen bonding between glutamines. The nature of interactions depends on pH [128]. Mineralization of dental lesions can be triggered by the attraction of calcium ions to the anionic charged components of glutamic acids [129].

Coassembly systems of peptide amphiphile (PA) molecules and growth factor β-1 (TGFβ-1) can form nanofibers for cartilage regeneration. It has been shown in a rabbit model that using these materials in conjunction with microfracture can successfully regenerate full-thickness articular cartilage. This material shows a route to develop synthetic bioactive biomaterial that can enhance the cartilage regeneration [130]. Several tissue engineering and regenerative medicine therapies designed for wound healing and orthopaedics applications have received Food and Drug Administration (FDA) clearance or approval and are commercially available (Table-2) [131].

TABLE-2
FDA-APPROVED REGENERATIVE MEDICINE

Category	Name	Biological agent	Approved use
Biologics	laViv	Autologous fibroblasts	Improving nasolabial fold appearance
	Carticel	Autologous chondrocytes	Cartilage defects from acute or repetitive trauma
	Apligraf, GINTUIT	Allogeneic cultured keratinocytes and fibroblasts in bovine collagen	Topical mucogingival conditions, leg and diabetic foot ulcers
	Cord blood	Hematopoietic stem and progenitor cells	Hematopoietic and immunological reconstitution after myeloablative treatment
Cell-based medical devices	Dermagraft	Allogenic fibroblasts	Diabetic foot ulcer
	Celution	Cell extraction	Transfer of autologous adipose stem cells
Biopharmaceuticals	GEM 125	PDGF-BB, tricalcium phosphate	Periodontal defects
	Regranex	PDGF-BB	Lower extremity diabetic ulcers
	Infuse, infuse bone graft, inductos	BMP-2	Tibia fracture and nonunion and lower spine fusion
	Osteogenic protein-1	BMP-7	Tibia nonunion

Self-healing smart surfaces: Just like living species, supramolecular assemblies can show self-healing property within a limit. They can repair themselves without any outside interference [132]. This inherent feature has rendered them as 'maintenance free' materials which can be utilized as adhesives, coatings and synthetic rubbers. Coatings on the surfaces protect them from any outside damaging condition but the conventional coatings like paints, resins and plastics often required to be re-applied to remove defects such as scratches. In this context, supramolecular architecture materials could be used as protective coatings with enhanced lifetime. The supramolecular aggregate polyrotaxane can be used to serve the purpose [133]. In rotaxane, a cyclic molecule is threaded onto an "axle" molecule and two terminals of axle are capped by bulky groups (Fig. 6A) [134]. Polyrotaxanes are polymers with multiple cyclic molecules threaded onto a polymer (Fig. 6B) [10,135]. Generally polyrotaxanes are comprised of cyclodextrins (CDs) as macrocycle and various linear polymers, especially poly(ethylene glycol) (PEG) as axle. Rotaxne can show excellent flexibility as the macrocycles can rotate freely around molecular axle due to the absence of any covalent bonding between the two. Over the last two decades, polyrotaxanes have been receiving increasing attention due to their fascinating supramolecular architecture and prospectus in bioapplications [136-140].

Polyrotaxane paints have been used by car manufacturing industries, specifically by Nissan (since 2005), to prevent the frequent repolishing the surface of the vehicles [133]. The same manufacturer has also applied supramolecular assembly to produce self-healing smartphone case, reported to be able to fix minor scratches within 1 h. According to Nissan, the outside paint contains polyrotaxane, which reacts to convert back to its original state and fill the gap, essentially repairing the defects when scratched by a fine object.

In batteries: In lithium-ion batteries silicon particles are used as an anode material, which increase its efficiency. However, the particle disintegration results in the lower battery lifetime as the significant volume changes occur in silicon during charge-discharge cycles [141]. To solve this problem, elastic materials traditionally polyacrylic acids are added as binder material. According to Choi and co-workers [142], the addition of 5% w/w polyrotaxane to the binder material leads to a great enhancement in elasticity due to ring sliding motion of polyrotaxane. Macrocyles can effectively dissipate energy by "sliding" along a molecular axle (Fig. 6B). By extending their lifespan, these high-capacity batteries could become economically viable.

Supramolecular separations of gold and other metals: For many years supramolecular and coordination chemistry are being applied in the extraction of metals such as copper,

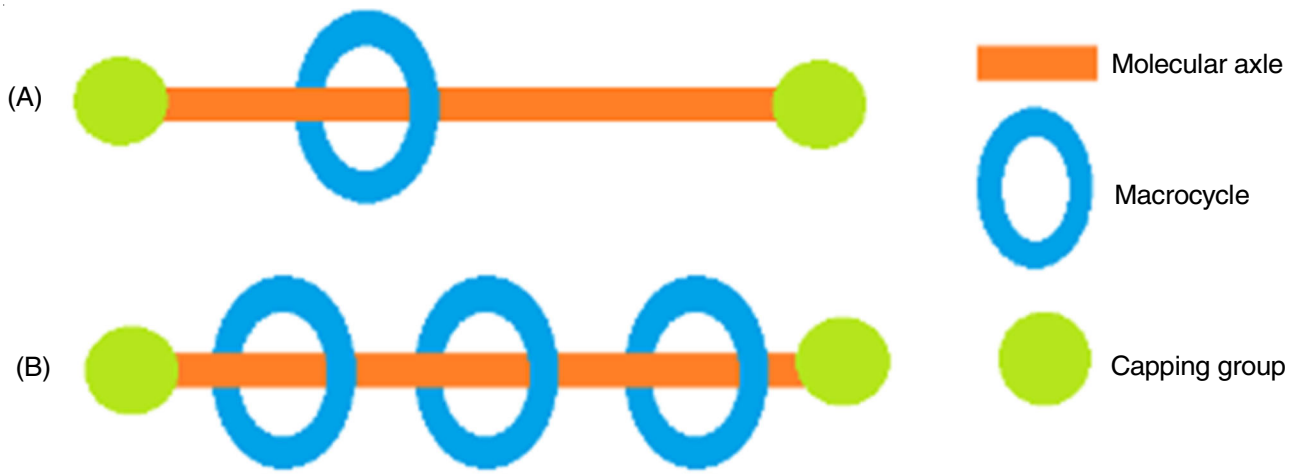

Fig. 6. (A) Rotaxane molecule (B) A polyrotaxane with multiple macrocycles

nickel, cobalt and zinc [143]. Recently supramolecular hosts have been utilized for the isolation of precious metals such as gold from waste electrical and electronic equipment (WEEE), such as mobile phones and computers [144,145]. The major targets of supramolecular separation are lowering the costs and reducing the use of highly toxic reagents such as cyanide. According to Tao *et al.* [146] cucurbit[8]uril (CB[8]) macrocycles can encapsulate $[AuCl_4]^-$ anions in honeycomb-like frameworks (Fig. 7). The presence of metal chlorides (M = Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}, Cu^{2+} and H_2PtCl_6) has no effect on this reaction if the precipitation was formed from hot solutions which is selective for $[AuCl_4]^-$ anions. Reusable metal and macrocycle mixtures could be produced by reducing gold in the framework with hydrazine. Haloaurate salts can also be encapsulated by α-cyclodextrin.

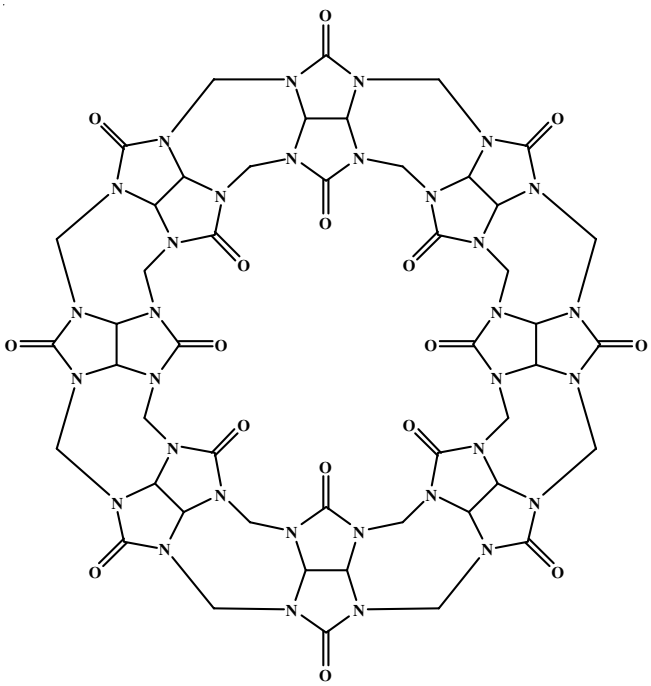

Fig. 7. Structure of cucurbit[8]uril (CB[8])

Cycladex has used supramolecular material in 2014, to reduce operating costs and toxic waste byproducts [147]. In this context, host–guest supramolecular chemistry has also been applied to extract radioactive cesium from high level nuclear waste. Walker *et al.* [148] developed ligand, calix[4]arene-*bis*-(*tert*-octylbenzo-crown-6) which can bind cesium from the waste streams (Fig. 8). They have also improved the resistance of solvent to thermal and radioactive decay. This process has been utilized by Oakridge National Lab to remove cesium from the Savannah river site (SRS).

Adhesive: Supramolecular chemistry has also been utilized in the production of many other simple household items. One example is superglue, a kind of cyanoacrylate adhesive. Cyanoacrylates have been used as fast setting, strong adhesives since 1950 [149]. According to McKervey *et al.* [150] if calix[4]arene tetraester (compound **1**, Fig. 9) or calix[6]arene hexaester (compound **2**, Fig. 9) is used in super glue, it accelerates the adhesion by sequestering group 1 metal cations. For example, addition of 0.1% compound **2** to a commercially available cyanoacrylate-based adhesive, fixture time can be reduced from 20-25 min to 3-5 min. This is because calixarene facilitates the bonding of porous surfaces prior to the diffusion of glue.

Room freshener: Supramolecular chemistry has also been utilized by Procter & Gamble in the production of a household product Febreze spray, which suppresses household bad odors and can also be applied on the fabrics [14]. Functionalized cyclo-dextrins are being used to serve the purpose. The major constituent of this Febreze spray is hydroxypropyl β-cyclodextrin (HPBCD) (Fig. 10), a cyclodextrin derivative which has enhanced solubility. It forms complex with odour molecules within the cavity of the macrocycle and reduces odors.

Conclusion

It seems to be remarkable that supramolecular materials that only emerged 55 years ago has already had such a significant effect on the world at large. Supramolecular chemistry as concept has just recently begun to be recognized for its potential in the commercial sectors. The potential of this emer-

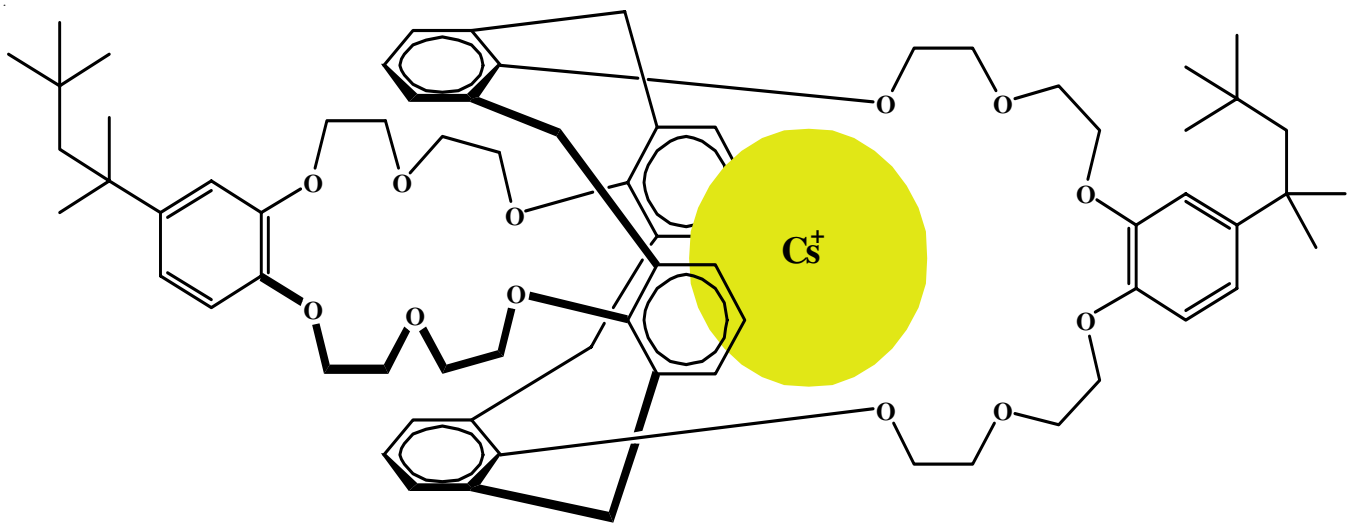

Fig. 8. Structure of calix[4]arene-*bis*-(*tert*-octylbenzo-crown-6) Cs extractant

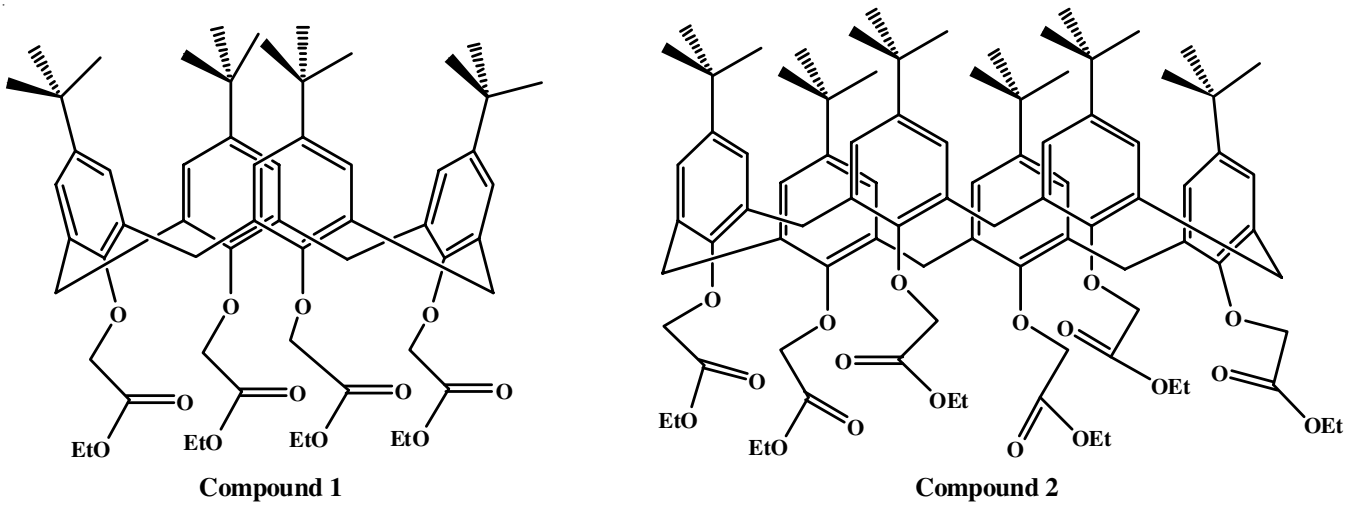

Fig. 9. Structure of calix[4]arene tetra-ester (compound **1**) and calix[6]arene hexa-ester (compound **2**)

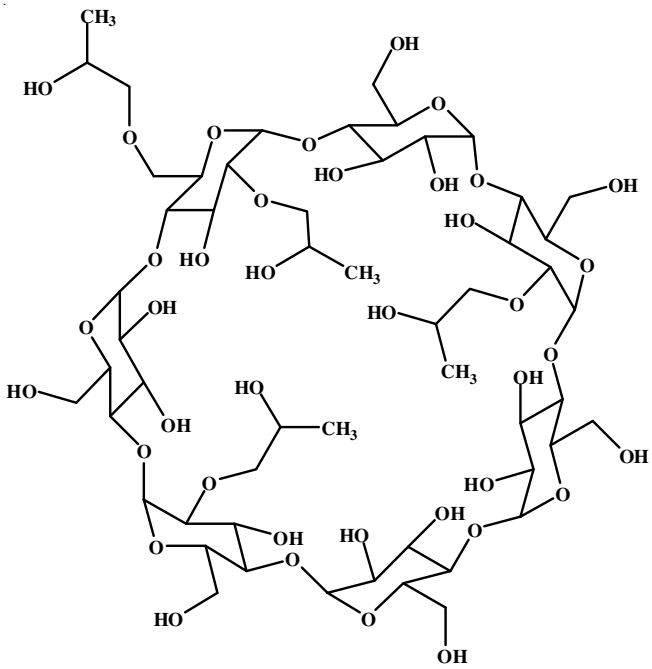

Fig. 10. Structure of hydroxypropyl β-cyclodextrin (HPBCD)

ging materials is set to be exploited in a wide variety of industrial scenarios. A few simple examples are covered in this overview to give readers a glimpse of supramolecular chemistry might influence in our daily lives. Several researchers are currently exploring the potential applications of supramolecular chemistry in areas as diverse as self-healing tyres, drug delivery vehicles and pharmaceutical sensors.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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