Review

Viswanathan S. Saji*

Supramolecular concepts and approaches in corrosion and biofouling prevention

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Abstract: Supramolecular chemistry is one of the exciting branches of chemistry where non-covalent interactions between molecules and the ensuing supramolecular structures have been studied for various applications. The present review provides a comprehensive outlook on the applications and potentials of supramolecular chemistry in corrosion and biofouling prevention. Reported works associating supramolecular chemistry with corrosion are systematically discussed under two sections: (i) surface coatings and (ii) corrosion inhibitors that include supramolecular polymers, host-guest inclusion compounds, organic-inorganic hybrid materials, and supramolecular structures of graphene, crown ethers, self-assembled monolayers, etc. Different strategies for making antifouling surfaces based on block copolymers/gel systems, host-guest systems, and metal-organic structures are briefed. Cyclodextrin and mesoporous silica-based host-guest systems are extensively discussed, as they are the most prominent materials of current research interest. Future potentials for developments are presented. The review is expected to be beneficial to enhance supramolecular chemistry-related research and development in corrosion and biofouling prevention.

Keywords: antibiofouling surface; corrosion inhibitor; host-guest systems; organic-inorganic hybrid materials; supramolecular chemistry; surface coating.

1 Introduction

Supramolecular chemistry, the “chemistry of molecular assemblies,” is a fascinating realm of modern science where researchers are constantly investigating the

possibilities of the design of novel supramolecular structures, surfaces, and techniques in different application areas including corrosion and biofouling prevention. Alternate definitions of supramolecular chemistry include “the chemistry of the intermolecular (non-covalent) bond” or “the chemistry beyond the molecule” or “nonmolecular chemistry.” Supramolecular species are branded by the three-dimensional (3D) arrangement of their constituents and by the nature of the intermolecular interactions [ion-ion, ion-dipole, dipole-dipole, hydrogen (H) bonding, π - π , cation- π , CH- π , van der Waals forces, close packing, coordination bonds, hydrophobic effect, etc.] (Steed & Atwood, 2000; Lehn, 2002). The bond strength of these intermolecular bonds ranges from $<5 \text{ kJ mol}^{-1}$ for van der Waals forces, $5\text{--}65 \text{ kJ mol}^{-1}$ for H bond, and up to 250 kJ mol^{-1} for an ion-ion interaction and is considerably weaker than that of a normal covalent bond ($\sim 350 \text{ kJ mol}^{-1}$ for carbon-carbon single bond) (Schubert et al., 2003). Multimolecular assemblies and complexes of natural molecules have been the main source of motivation for supramolecular chemists. Since the earlier reports on the supramolecular organization (Powell, 1948), a large number of works have been reported on supramolecular structures for different applications including sensors, biomedical systems, and smart stimuli-responsive systems (Lehn, 1995; Szejtli & Osa, 1999; Atwood & Steed, 2004; Atwood et al., 2017).

Supramolecular compounds can be conveniently classified into (i) molecular self-assemblies, (ii) host-guest complexes, and (iii) molecules built to specific shapes (rotaxanes, dendrimers, etc.). A supramolecular *self-assembly* can be defined as the spontaneous organization of a few or many components forming structurally well-defined supramolecules through non-covalent interactions in a given set of conditions. In the *host-guest* (molecular recognition – a molecule recognizing a partner molecule) chemistry, a host (a large molecule, an aggregate, or a cyclic compound possessing cavity) binds a guest (another molecule) yielding a host-guest complex (supramolecule). They are also known as inclusion/occlusion/addition compounds. The host systems can be classified into cavitands (hosts possessing intramolecular cavities; examples include crown ethers and spherands)

*Corresponding author: Viswanathan S. Saji, Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia, e-mail: saji.viswanathan@kfupm.edu.sa

and clathrates [hosts possessing extra-molecular cavities, usually a gap between two or more hosts; examples include calixarene and cyclodextrins (CDs)]. This fascinating arena of research has won the 1987 Nobel prize for Pedersen, Cram, and Lehn. More details on the topic are available elsewhere (Lehn, 1990, 1993, 1994, 2009, 2017; Gale, 2000; Menger, 2002; Oshovsky et al., 2007; Winter et al., 2012; Reinhoudt, 2013; Huang & Anslyn, 2015; Resnati et al., 2015; Teyssandier et al., 2016).

Corrosion is an inevitable devil and causes material destruction and component failures. The worldwide cost of corrosion is projected to be US\$ 2.5 trillion, which is comparable to 3.4% of the global gross domestic product (Saji & Cook, 2012; Popoola et al., 2013; Koch et al., 2016). By and large, corrosion can be controlled by proper amendments in the material (e.g. corrosion-resistant alloys), the environment (e.g. corrosion inhibitors), or the material's surface (e.g. coatings) (Saji & Cook, 2012). Protective surface coatings prevent corrosion of the underlying substrate based on either barrier protection (passive coatings) or active protection (corrosion inhibitors incorporated) (Saji & Thomas, 2007; Hughes et al., 2010; Raja et al., 2010). The concept of smart coatings combines both the active and the passive protection smartly by releasing the inhibitors on demand (see § 2). For more details on the fundamentals of corrosion and methods of control, the reader is referred to bonafide textbooks (Fontana & Greene, 1985; Uhlig & Review, 2008). A number of recent reviews can be found in the present journal emphasizing the importance of novel approaches in corrosion

(Eliaz & Latanision, 2007; Taylor et al., 2007; Chiba et al., 2018; Gergely, 2018; Roselli et al., 2018).

Corrosion issues in industries are often correlated with fouling issues (inorganic and biofouling) and pose immense threats to the material's safety (Reg Bott, 2011). More descriptions on biofouling are provided in § 4.

Despite the extensive history of Corrosion Science and Technology, no comprehensive attempt has been made to systematically address the application of supramolecular chemistry in corrosion prevention strategies. Most of the reviews and books available in this area are on smart coatings (see § 2). A few reviews on polymer/sol-gel/superhydrophobic coatings mentioned different supramolecular interactions (see § 2 and 3). No reviews addressed supramolecular structures for corrosion inhibition. The present work made an effort in this direction where research advancements in corrosion prevention strategies based on supramolecular chemistry are systematically classified and presented in a simple manner (Figure 1). Also, an account on the current research on supramolecular approaches for fabricating antibiofouling surfaces is presented (see § 4), where interesting recent advancements are discussed. Works reported on inorganic-organic hybrid structures [metal-organic frameworks (MOFs), coordination polymers, etc.] (Biradha et al., 2009) are also incorporated, as they form a subset of supramolecular chemistry, the dynamic covalent chemistry (Jin et al., 2013). There is no significant information available on supramolecular chemistry in cathodic protection or inorganic antifouling applications.

Figure 1: Chart showing the application areas of supramolecular chemistry in corrosion and biofouling prevention as presented in this review.

2 Surface coatings

Supramolecular concepts have been utilized in organic, inorganic, and organic-inorganic hybrid coatings. This section describes recent research advancements where supramolecular approaches are used in designing more efficient surface coatings.

2.1 Supramolecular polymers

A supramolecular polymer can be defined as a short chain organic material that is held together by non-covalent interactions, for instance, H bonding (Schmuck & Wienand, 2001; Park & Zimmerman, 2006), host-guest chemistry (Harada et al., 2009; Guo & Liu, 2012), metal coordination (Burnworth et al., 2011; Haino et al., 2012), or π interaction (Hill et al., 2004; Song et al., 2007), exhibiting strength and stiffness similar to traditional covalent bonded polymers (Brunsveld et al., 2001; Bouteiller, 2007). In a broader sense, the term supramolecular polymer is also used for self-organized macromolecules of conventional polymers using non-covalent interactions (Žigon & Ambrožič, 2003). They can form stacks, micelles, polymersomes, dendrimers, or 3D cross-linked polymer networks (Berg & Loose; Qi & Schalley, 2014). They are widely investigated in different applications such as liquid crystalline materials, light harvesting systems, smart materials, thermoplastic elastomers, and biomedical materials (Fouquey et al., 1990; Brunsveld et al., 2001; Tellini et al., 2006; Aida et al., 2012; Armao IV et al., 2017).

A few works on supramolecular polyurethanes (PUs) in developing self-healing anticorrosion coatings are available. Even though reported works on supramolecular structures of PUs are available since the 1970s (Yablokov et al., 1970), only a few reports are dedicated to their application in corrosion prevention coatings (Ciesielski et al., 2009; De Cat et al., 2011), and this can be primarily due to the predictable inferior barrier properties. It is accepted that the barrier properties of polymer coatings are primarily attributed to the covalent bonding. The complete replacement of covalent interactions with non-covalent interactions, hence, can be detrimental for corrosion protection. On the other hand, supramolecular polymers are advantageous with regard to processability, self-healing capability, and recyclability owing to their monomer-polymer reversible transitions (Folmer et al., 2000) (see § 2.2). Recent studies have shown that partial replacement of covalent bonding with non-covalent interactions can provide self-healing properties without losing the barrier

effect. Deflorian et al. reported a novel supramolecular PU coating where covalent bonds were partly replaced with non-covalent H bonds; this provided self-healing properties in the coating owing to the reversibility of the non-covalent interactions. The study evaluated the synergistic action of the self-healing ability and barrier properties on damaged (scratched) coatings. Their electrochemical impedance spectroscopy (EIS) studies clearly showed that the barrier properties are certainly associated with the covalent bond network. However, partial replacement of covalent bonds (up to ~25%) does not destructively affect the barrier properties of the resins. The work demonstrated the possibility of using multiple H bonds in coatings, as it can provide self-healing and, hence, protection from corrosion (Deflorian et al., 2013).

One disadvantage of the supramolecular polymers is the comparably lower stability at stimulated conditions of heat or light. Hence, different efforts are ongoing to make supramolecular composites where suitable additives/fillers are used to overcome the drawbacks. Such materials can offer better mechanical properties and are attractive for tough, corrosion-resistant, and healable coatings (Lin et al., 2017). Leon et al. patented a bituminous polyolefin composite capable of forming supramolecular assembly comprising one or more associative groups for waterproofing coatings (Leon & Barreto, 2014). More details are provided in the subsequent sections.

2.2 Nano/microcontainers in coatings

Structural transitions of supramolecular assemblies allow stimuli responsiveness, which can be used for on-demand release smart coatings. When compared to the direct incorporation of the corrosion inhibitor in a coating, encapsulating them in suitable nanocontainers can yield better results and can avoid probable “inhibitor-coating matrix” adverse reactions. The nanocontainers dispersed in primers can release the encapsulated inhibitors in a controlled way, which can be adjusted to happen together with the corrosion initiation or local environment changes (temperature/pH/pressure changes, radiation, mechanical action, etc.) by utilizing reversible covalent bonds or weaker non-covalent interactions. Smart coatings can be classified based on functionalization, which can have multiple functions such as self-cleaning, self-healing, antibiofouling, and anticorrosion. More details on smart coatings can be found elsewhere (Schubert et al., 2003; Zheludkevich et al., 2007; Shchukin et al., 2008; Baghdachi, 2009; Esser-Kahn et al., 2011; Hollamby et al., 2011; Ariga et al., 2012; Barthes et al., 2012; Saji & Cook, 2012;

Zheludkevich et al., 2012; Shchukin & Möhwald, 2013; Falcón et al., 2014; Makhlof, 2014; Montemor, 2014; Wei et al., 2015; Stankiewicz & Barker, 2016; Zahidah et al., 2017; Nazeer & Madkour, 2018; Zhang et al., 2018a).

Many research efforts are currently underway in preparing supramolecular corrosion inhibitor nanocontainers. Porous, hollow, or layer-structured materials/assemblies are often chosen for this purpose. § 2.2.1 to 2.2.4 briefly explain the advancements in this area. Among them, supramolecular concepts are majorly utilized in the host-guest systems (§ 2.2.2). Other sections are briefed.

2.2.1 Polymeric capsules

Polymeric micro/nanocapsules have been investigated widely as carriers of core materials. Here, the active constituent (core) is packed within another material (shell) to guard the core from the immediate environment. Either monomers/prepolymers (by methods such as emulsion polymerization, suspension polymerization, interfacial polycondensation, etc.) or polymers (by suspension cross-linking, solvent extraction, etc.) can be utilized for the fabrication of micro/nanocontainers. Other micro-encapsulation methods include extrusion, spray drying, coacervation, precipitation, and sol-gel. A common, easy method is the in situ polymerization, oil-in-water emulsion (Shukla, 2006), where the polymerization process propagates on the core material droplet, yielding a solid polymeric shell. Polyurea (PUA)-formaldehyde containers are one of the first strategies developed in this area (White et al., 2001). PU is a commonly employed material. More details on polymeric nanocontainers are described elsewhere (Abu-Thabit & Makhlof, 2015; Wei et al., 2015).

Latnikova et al. developed a method to encapsulate inhibitors by interfacial polymerization with three different high cross-link density polymers [PU, PUA, and polyamide (PA)]. It was found that the type of polymer had a significant impact on the structure of the capsules formed. The PU and PUA compact particles loaded with the inhibitors were found to be homogeneously disseminated in the polymer matrix when compared with the PA capsules (Latnikova et al., 2012). Gite et al. fabricated PUA microcapsules with quinoline incorporation. Well-defined, thermally stable (up to 200°C) globular microcapsules with mean diameters of 72 and 86 μm were obtained when xylene and ethyl acetate solvents were used, respectively. Ultraviolet (UV) spectroscopy and weight loss studies showed that the release rate from the PUA microcapsules was higher when xylene solvent was used. Electrochemical corrosion studies revealed that a corrosion rate as low

as 0.65 mm year⁻¹ was obtained for a PU coating loaded with 4 wt.% of polymer capsules containing quinoline corrosion inhibitor for mild steel in 5 wt.% HCl (Gite et al., 2015). Huang et al. fabricated PU microcapsules encompassing hexamethylene diisocyanate (core material) via interfacial polymerization of methylene diphenyldiisocyanate prepolymer and 1,4-butanediol in an oil-in-water emulsion. The encapsulation occurs in situ synchronously with polymeric shell formation. Their accelerated corrosion studies showed significantly improved performance for the self-healing coating (Huang & Yang, 2011).

Li et al. reported pH-responsive polystyrene (PS) as a polymeric nanocontainer loaded with corrosion inhibitors for anticorrosion coatings. Corrosion inhibitors [benzotriazole (BTA)] are captured in the PS matrix during polymerization, which was succeeded by the adsorption of a highly branched polyethylenimine as a controlled release system of BTA to external pH (Li et al., 2014). Kakaroglou et al. studied encapsulated sodium molybdate inhibitor for steel in brackish water. Capsules (inhibitor reservoirs, $\sim 10 \mu\text{m}$) that consisted of PUA and PU were prepared as a result of the reaction of isocyanates with H₂O of the emulsion and the surfactants, and were well distributed over the thickness of the coating. The PU coating with the incorporated capsules showed remarkably improved corrosion resistance; however, the long-term salt spray studies presented decreased barrier performance after 360 h, which was suggested to be due to the high solubility of the molybdate inhibitor (Kakaroglou et al., 2016). Maia et al. reported assembly of PUA microcontainers loaded with 2-mercaptobenzothiazole (MBT). Corrosion studies of the microcapsule-incorporated hybrid sol-gel coating on the 2024 Al alloy showed that the MBT encapsulated capsules did not affect the coating's barrier properties, and an improvement in coating adhesion was observed (Maia et al., 2016). Latnikova et al. reported an interesting concept by the synergistic action of the passivation effect and hydrophobicity where alkoxysilanes having long hydrophobic tails were encapsulated in PU microcapsules. On coating damage, the released alkoxysilanes form a covalent interaction with the -OH groups on the metal surface, resulting in an inactive electrochemical film formation. The hydrophobicity attributed to the long hydrocarbon tails improved the barrier properties of the film by preventing penetration of H₂O and aggressive ions. Their scanning vibrating electrode technique (SVET) studies showed enhanced corrosion prevention by the coated substrate in 0.1 M NaCl (Latnikova et al., 2011). A recent review on polymeric nanocontainers is available where comprehensive details can be found (Wei et al., 2015). Details on supramolecular polymers such as CDs are presented in the next section.

Replacement of the capsules with microgels has been widely investigated. An example of such a system is the PUA microgel particles containing 2-methylbenzothiazole (Cai et al., 2011; Cécile et al., 2018). More details on microgel coatings are discussed in § 4.

2.2.2 Host-guest complexes

Stimulus feedback anticorrosion coatings, fabricated by the dissemination of “guest” materials (embedded smart nanocontainers loaded with inhibitors) into “host” matrix (e.g. sol-gel or polymer barrier coating), have attracted much research attention. The guest component is a nanoscale container with adjustable voids or tailored surfaces where the inhibitors can be encapsulated. The expected properties of the guest are its high loading capability, compatibility with the system, stimulus responsiveness, controlled release, zero premature release (before corrosion starts), and prompt high sensitivity. The extent of the nanocontainers in the coating needs to be adjusted without affecting the coating barrier effect. Literature analysis revealed that most of the recently reported works utilized host-guest chemistry based on mesoporous silica or CDs. More details on the fundamentals of the host-guest coatings are described somewhere else (Shchukin et al., 2006; Shchukin & Möhwald, 2007a; Saji & Cook, 2012; Makhoulouf, 2014; Montemor, 2014; Popoola et al., 2014; Wei et al., 2015; Stankiewicz & Barker, 2016; Ding et al., 2017; Zahidah et al., 2017).

2.2.2.1 Mesoporous silica based

Mesoporous silica nanocontainers (MSNs) have enticed significant research attention due to their large specific surface area, easy surface functionalization, biocompatibility, high stability, and controllable pore diameter (Nguyen et al., 2006; Ruiz-Hernández et al., 2007; Chang et al., 2010; Vivero-Escoto et al., 2010; Maia et al., 2012; Wei et al., 2015; Zhao et al., 2017). Borisov et al. investigated a silica-zirconia sol-gel coating doped with BTA-loaded MSNs, and the study revealed that the MSNs could be inserted with high inhibitor loading and can provide superior anticorrosion efficiency. The mechanically stable nanocarriers were distributed homogeneously throughout the coating, blocked micropores, and cracks and demonstrated improved barrier properties (Borisova et al., 2011). The authors in subsequent works showed that lower (0.04 wt.%) concentrations of embedded nanocontainers in the coating led to good barrier properties, but poor corrosion inhibition due to inhibitor

deficiency. In contrast, higher concentrations of the nanocontainers (0.8–1.7 wt.%) resulted in coating degradation, introduced diffusion paths, and resulted in a decreased barrier effect. The EIS and SVET studies showed that a 0.7 wt.% MBT-MSNs-incorporated coating exhibited the best active/passive corrosion protection (Borisova et al., 2012, 2013). Zheludkevich et al. reported a layer-by-layer (LbL) assembly where pH-sensitive silica nanoparticles were covered with polyelectrolyte and BTA layers, which was subsequently assimilated into a sol-gel-derived hybrid film [a SiO_2 /PEI/PSS/BTA/PSS/BTA layer structure where PEI and PSS corresponds to poly(ethylene imine) and poly(styrene sulfonate), respectively]. The inhibitor (BTA) loading was ~95 mg/1 g of SiO_2 particles. The EIS measurements demonstrated better corrosion resistance for the nanocontainer-embedded coating when compared to the bare coating and the active coating with direct inhibitor impregnation (without nanocontainers). The enhancement was attributed to the improved adhesion, the additional barrier effect of nanocontainers, and the slow inhibitor release. When corrosion initiated, the local pH changed and, hence, opened the polyelectrolyte shell of the nanocapsules releasing BTA. Once corrosion suppressed, the local pH recovered, and thereby the polyelectrolyte shell closed (Zheludkevich et al., 2007).

Chen and Fu synthesized hollow mesoporous silica (HMS) nanocontainers via poly(vinylpyrrolidone) and cetyltrimethylammonium bromide templates, and subsequently, supramolecular nanovalves (pH-sensitive) comprising cucurbit[6]uril (CB[6]) rings and bisammonium stalks were anchored to the HMS' exterior surface. At neutral pH, the CB[6] encompassed the bisammonium stalks firmly (nanopore openings closed), and once the pH augmented, deprotonation of the stalks and de-threading of the CB[6] occurs (nanopore openings disclosed with inhibitor release) (Figure 2A). The synthesized HMSs were spherical in shape with diameters ranging from 0.5 to 0.8 μm , and the shell thickness was ~100 nm (Figure 2). The fabricated HMSs were initially functionalized with 3-chloropropyltriethoxysilane (CPTES) and subsequently treated with 1,4-butanediamine (BDA) to make intact stalks on the surface. Afterward, the inhibitor (BTA) and the CB[6] were added to fabricate HMSs with pH-responsive nanovalves (Figure 2B). The pH-controlled release profile of the inhibitor showed two distinct regions: the quick release and the sustained-release areas. The assembled HMS design was found to be helpful in preventing the unwanted inhibitor leakage in neutral pH (~1.5% of BTA leaked for 120 min). At neutral conditions, the protonated BDA units can produce firm inclusion complexes with CB[6] through ion-dipole and hydrophobic interactions.

Figure 2: (A) Schematic illustration showing the operation of pH-responsive nanovalves. (Right) TEM and SEM images of HMSs. (B) The assembly process of HMSs where the steps correspond to (i) CPTES, dry toluene, reflux/95°C/24 h, (ii) BDA, dry toluene, reflux/12 h, and (iii) BTA, acetone, 24 h; then CB[6], NH₄OAc buffer solution, pH 6.5, 24 h (reproduced with permission from Chen & Fu, 2012a; Copyright @ IOP Science).

At higher pH ranges, the originally protonated BDA units were partly or completely deprotonated, causing dissociation of the supramolecular complexes (Chen & Fu, 2012a). The authors in a related work reported acid-responsive HMSs based on α -CD/aniline complex in a sol-gel coating (Chen & Fu, 2012b).

Ding et al. investigated a novel organic silane-based corrosion potential-stimulus feedback active coating (CP-SFAC) for magnesium (Mg) alloys, based on the redox-responsive self-healing concept (surface potential drop after localized corrosion onset was exploited as the trigger) (Ding et al., 2016, 2017). The design utilized corrosion potential-stimulus responsive nanocontainers (CP-SNCs) that are composed of Fe₃O₄@mSiO₂ as magnetic nanovehicles and bipyridinium $\subset$ water-soluble pillar[5]arenes (BIPY $\subset$ WP[5]) assemblies as gatekeepers/disulfide linkers. The Fe₃O₄@mSiO₂ synthesized by the reverse microemulsion method showed a core-shell structure with ~50-nm-thick amorphous SiO₂ shell. The Brunauer-Emmett-Teller (BET) surface area, pore volume, and Barrett-Joyner-Halenda (BJH) pore diameter of Fe₃O₄@mSiO₂ were 572.6 m² g⁻¹, 0.97 cm³ g⁻¹, and 2.49 nm, respectively. The made-up CP-SNCs were subsequently assimilated into a sol-gel hybrid coating and coated on an AZ31B alloy (CP-SFAC). At corrosion potentials (−1.5 V vs. SHE, Mg alloy), the inhibitor

gets released promptly because of the cleavage of disulfide linkers and the removal of the supramolecular assemblies. CP-SFAC displayed excellent anticorrosion performance in 0.1 M NaCl with rapid self-healing capability. Shortening the distance between the CP-SNCs and the alloy surface was found to enhance its availability, which was helpful to timely respond to the corrosion potential-stimulus (Ding et al., 2017).

Even though the supramolecular functionalization helps to avoid the premature leakage of the inhibitor, it is difficult to prevent them completely. Zheng et al. reported an effective prevention strategy for premature leakage through organosilyl modification at the outlet of mesopores that also enhanced adhesion of the containers with the host matrix. The authors synthesized en-(COO⁻)-MCM-41 and en-(COO⁻)₃-MCM-41 by the post-functionalization reaction between silica and N-(3-trimethoxysilylpropyl)-ethylenediamine or N-(trimethoxysilylpropyl)-ethylenediamine triacetic acid trisodium salt in reflux of toluene (where MCM-41 and en correspond to silica nanoparticles and silylpropyl-ethylenediamine, respectively). The functionalized silica nanoparticles (FSNs 2–6), having a pseudospherical shape (Figure 3), were intact with diameters at the range of 70–90 nm and showed only minor enlargement when compared with MCM-41. The porosity

Figure 3: (Left) TEM and SEM images of FSN 4 (A, B) and FSN 5 (C, D) (scale bar: TEM, 100 nm; SEM, 200 nm). (Right) N₂ sorption isotherms (A) and pore diameter distribution (B) for MCM-41 (I), FSN 2 (II), FSN 4 (III), FSN 5 (IV), and FSN 6 (V). (C) The uptake and release capacities of the nanocontainers by TGA and UV-vis, respectively. (D) Release profile plots of BTA from loaded native MCM-41 (I), FSN 2 (II), FSN 4 (III), FSN 5 (IV), and FSN 6 (V) at neutral pH (reproduced with permission from Zheng et al., 2015; Copyright @ The American Chemical Society).

as evaluated by N₂ sorption showed a type IV isotherm (Figure 3A). Native MCM-41 displayed a sharp adsorption step at intermediate P/P_0 values (between 0.2 and 0.4), suggesting its potential capability for inhibitor loading. Functionalized FSNs exhibited diminished isotherm plateau, consistent with the pore volume shrinkage (ca. 30%), which indicated a reduced theoretical uptake amount of the inhibitor. Also, the pore diameter of the native MCM-41 gets reduced by ~1 nm after the treatment with the en groups (peak II, Figure 3B). It is further reduced to 2.5 nm after carboxylation (peak III). As shown in Figure 3C, the native MCM-41 exhibited the maximum BTA loading of 34.5 wt.%, which corresponds to the largest pore volume. The uptake capacities were similar between FSN 4 and FSN 5, which were marginally lower than that of FSN 2 (27.2 wt.%). Figure 3C and D also unveiled that the release capability of FSN 2 was only 60% of the total loaded inhibitor, which indicated a noteworthy interaction between the diamine groups and the guest molecules. The electrostatic attraction between the negatively charged BTA (dissociation of 1H-BTA, $pK_a=6.64$) and the $-NH_3^+$ groups (on the inner wall and orifice of mesopores) retarded the inhibitor release. The native MCM-41, FSN 4, and FSN 5, on the other hand, can release 80% of the stored inhibitors and at higher release rates. The nanocontainer-incorporated coating showed good barrier effect, long-term self-healing effect, and stimuli responsiveness to local pH change (Zheng et al., 2015).

Zhao et al. fabricated hollow silica nanocapsules with magnesium hydroxide (inorganic salt) precipitation in shells (HSNs-M) through an inverse emulsion polymerization where the inhibitor, BTA, has been captured in HSNs during the process of polymerization (HSNs-M/BTA). Thermogravimetric analysis (TGA) showed that the inhibitor loading was 287.17 mg/1 g (HSNs-M/BTA), whereas the corresponding loading in HSNs without salt precipitation was 520.68 mg. UV-vis spectroscopic release studies at different pH values showed that the inhibitor release could be initiated by pH change. The amount of released BTA from the salt-precipitated HSNs in acidic solution (~2.21 mg l⁻¹) was significantly higher than that of the HSNs without salt precipitation. EIS and Tafel analysis showed that the HSNs-M/BTA-incorporated coating possesses good anticorrosive protection for Al in 0.1 M NaCl, which was correlated to the controlled inhibitor release and improved surface hydrophobicity. Despite the lower inhibitor loading, the formation of magnesium hydroxide precipitates in shells was found to be helpful in providing long-term corrosion protection due to the slow rate of release of inhibitors in neutral and alkaline pH. At acidic pH, the prepared HSNs-M/BTA immediately released a few amounts of BTA and inhibited corrosion initiation (Zhao et al., 2017).

Redox-triggered smart nanocontainers (RTSNs), assembled by mounting supramolecular switches (β -CD functionalized with ferrocene) onto the external surface of MSNs, were reported by Wang et al. With a redox

stimulus, a reversible transition from self-complexation to self-dissociation of the supramolecular switches happens, which controls the inhibitor (p-coumaric acid, CA) release encapsulated in the MSNs. A bi-layered nanocomposite coating [fabricated by consecutive deposition of (i) Ce(IV)-doped $\text{ZrO}_2\text{-SiO}_2$ and (ii) RTSN-incorporated $\text{ZrO}_2\text{-SiO}_2$ coatings] on the AA2024 Al alloy showed higher barrier performance and efficiently deferred corrosion initiation on the Al alloy (in 0.5 M NaCl, 20 days). On coating damage, Ce(IV) salt met with RTSNs in the scratched area and opened the supramolecular switches, resulting in the release of the inhibitor. Meanwhile, Ce(IV) was reduced to Ce(III) (Wang et al., 2017a).

Liang et al. reported a facile one-step technique to assemble acid and alkali dual-stimuli-responsive SiO_2 -imidazoline (IMI) nanocomposites (SiO_2 -IMI) with high inhibitor (1-hexadecyl-3-methylimidazolium bromide) loading capacity. The SiO_2 -IMI were homogeneously dispersed into the hydrophobic SiO_2 sol, and a host-guest feedback active coating with a superhydrophobic surface (SiO_2 -IMI@SHSC) was realized on the AA2024 Al alloy by dip coating where the presetting down- and up-steps were reiterated four times to attain a coating thickness of $\sim 1.0\ \mu\text{m}$. The hydrophobic SiO_2 sol doped with SiO_2 -IMI was used only for the first-round dipping to concentrate SiO_2 -IMI near the metal surface. SiO_2 -IMI@SHSC presented a superhydrophobic surface, having a water contact angle of 150.5° . Notably, the random accumulated hydrophobic SiO_2 nanoparticles improved the root-mean-square surface roughness, which was calculated as 51 nm by atomic force microscopy (AFM) and was helpful in enhancing the surface hydrophobicity. SiO_2 -IMI@SHSC displayed a decent long-term anticorrosion performance in 0.5 M NaCl, attributed to the superhydrophobic and self-healing active corrosion protection by the assimilated SiO_2 -IMI (Liang et al., 2016).

2.2.2.2 CD based

The cyclic oligomers of glucose recognized as CDs are one of the main supramolecular hosts that can provide different

self-assembled structures and functionalities. CDs are attractive due to their availability, biocompatibility, and cost factor (Szejtli, 1998; Szejtli & Osa, 1999). Table 1 and Figure 4 compare the interesting properties of key members of the CD family (α -, β -, and γ -CDs). CDs consists of six to eight D-glucopyranoside units connected edge to edge, with the faces pointing inward, and headed for a central hydrophobic cavity wherein the internal cavity can accommodate guest molecules (Saenger, 1980; Raymo & Stoddart, 1997). Their interior surface is hydrophobic, whereas the external surface is hydrophilic (Rekharsky & Inoue, 1998; Engeldinger et al., 2003). The well-documented ability of CDs to form host-guest compounds has been exploited in different directions including the CD-based rotaxanes and pseudorotaxanes (Stoddart, 1992; Collier et al., 2001) and has been investigated for a number of applications (Patra et al., 2013; Chen et al., 2016; Xiong et al., 2017).

Amiri and Rahimi used the α , β , and γ forms of a CD-based inclusion complex containing organic inhibitors [MBT or 2-mercaptobenzimidazole (MBI)] to create on-demand release anticorrosion coating. The formation of inclusion compounds was characterized by proton nuclear magnetic resonance ($^1\text{H-NMR}$), X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry, and Fourier-transform infrared spectroscopy (FTIR), where the hydrophobic cavity of the CD has encapsulated the benzyl part of the MBT/MBI. The salt spray test revealed that a larger size of a nanocapsule, a higher nanocapsule content, and a thicker coating afforded improved corrosion protection. Corrosion initiation of the coated Al substrate occurred after 6 days of salt spray on the bare sample and increased with increase in exposure time, but the samples with the nanocontainer-based coatings did not rust even after 1000 h. Figure 4C shows a typical result of the salt spray test, which was supported by their electrochemical measurements in 5% NaCl (Amiri & Rahimi, 2015; Rahimi & Amiri, 2016).

A functional nanoreservoir based on multi-walled carbon nanotubes (MWCNTs) and β -CDs was produced via a novel and simple chemical process. The SEM analysis

Table 1: Properties of different forms of CDs (reproduced with permission from Rahimi & Amiri, 2016; Copyright @ Springer).

Property	α -Cyclodextrin	β -Cyclodextrin	γ -Cyclodextrin
Number of glucopyranose units	6	7	8
Molecular weight (g/mol)	972	1135	1297
Solubility in water at 25°C (w/v%)	14.5	1.85	23.2
Outer diameter ($\text{\AA}$)	14.7	15.3	17.5
Cavity diameter ($\text{\AA}$)	5.1	6.2	8.1
Height of torus ($\text{\AA}$)	7.8	7.8	7.8
Cavity volume ($\text{\AA}^3$)	174	262	427

Figure 4: (A) Molecular structure of CDs. (B) Schematic showing formation of an inclusion complex with guest molecule. (C) Results of the 1000-h salt spray test of coated Al alloy (reproduced with permission from Amiri & Rahimi, 2014, 2015; Rahimi & Amiri, 2016; Copyright @ Springer).

revealed that there was a notable expansion of MWCNTs after being modified by β -CD, which indicated that β -CD was mounted on the surface of the MWCNTs. The transmission electron microscopy (TEM) images showed that it was an assembly of individual MWCNTs with heterogeneous layers on the surface, which was consistent with the results of the XRD, FTIR, TGA, and BET. The β -CD/MWCNTs were subsequently loaded with a benzimidazole inhibitor and blended into epoxy as a filler to augment its anticorrosion performance. A scarification test in NaCl solution for 12 h supported the anticorrosion and self-healing capabilities, which were ascribed to the controlled inhibitor release. The EIS studies suggested that despite the decreased barrier property of the coating with time, the encapsulated corrosion inhibitor played a significant role in metal protection (He et al., 2016). More works on CDs are described in § 3 and § 4.

2.2.3 Inorganic clay-based nanocontainers

As a low-cost nanocontainer, several investigations were made on halloysite clay nanotubes. Selective alterations of halloysite surfaces (inner and outer) can be realized by manipulating supramolecular interactions. The strong surface charge of halloysite tubules can allow multilayer

assemblies at the nanoscale through LbL adsorptions, which can be covered with polyelectrolytes to form nano-shells, blocking the tube ends and achieving controlled release of encapsulated inhibitors. The release can be regulated by an external stimulus (e.g. pH changes), as the polyelectrolyte multilayers are sensitive to changes in the surrounding environment (Abdullayev et al., 2009). Studies have suggested that their main drawback is low loading efficiency (Borisova et al., 2012, 2013). In addition to the carriers of corrosion inhibitors, the halloysite nanotubes (HNTs) can be utilized as a reinforcing filler for barrier coatings. Several good reviews and books are available on this topic (Shchukin & Möhwald, 2007b; Lvov et al., 2008; Shchukin et al., 2008; Abdullayev et al., 2009; Fix et al., 2009; Zheludkevich et al., 2010; Falcón et al., 2015; Zahidah et al., 2017; Lazzara et al., 2018).

Falcon et al. reported the EIS and SVET results for carbon steel coated with a primer layer doped with dodecylamine (DAM) inhibitor-loaded HNTs (10 wt.%). The coating showed self-healing capability by the release of the captured DAM initiated by pH variations. The nanotubes were subjected to a pre-treatment (before inhibitor loading) in $2 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ for 6 and 12 h. The pre-treatment was found to improve tube-loading efficiency and henceforth the inner space availability for encapsulation. Carbon steel panels were coated with a commercial

alkyd paint modified with 10 wt.% of DAM-loaded HNTs as a primer layer (94- μm dry thickness) and subsequently with a second layer ($\sim 99\ \mu\text{m}$) without HNTs. The kinetics of the inhibitor release as a function of pH was studied by EIS. Bode plots of the two-layer-coated sample containing 0 and 10 wt.% of HNTs in the primer showed a capacitive response extending from high to medium frequencies, indicating defect-free coating. The addition of HNTs caused only a marginal decrease in impedance modulus at low frequencies, indicating that HNTs do not affect the properties of the coating barrier markedly. This was attributed to the small size and good dispersion of HNTs in the paint, which prevented possible agglomeration and hence permitted homogeneous dissemination in the coating layer. The salt spray test after 720 h showed severe corrosion on the coated samples without HNTs, whereas the coated samples with 10 wt.% of DAM-loaded halloysite showed fewer corrosion products with no blistering around a scribe, avoiding the spread of under-paint corrosion (Falc3n et al., 2015).

A number of studies on layered double hydroxides (LDHs) or anionic clays that comprise stacks of positively charged layers of mixed-metal hydroxides, stabilized by anions and solvent molecules are available. More details on LDHs are described elsewhere (3lvarez et al., 2010; Rosero-Navarro et al., 2010; Tedim et al., 2010; Zheludkevich et al., 2012; Figueira et al., 2016). It is well known that inorganic clays, such as montmorillonite, were widely employed in nanocomposite coatings to improve the physical and rheological properties of polymers (Zamanizadeha et al., 2015). Hence, clay-based stimuli-responsive coatings with optimized nanocontainers are expected to be good in terms of both self-healing and barrier layer properties.

2.2.4 Polyelectrolyte multilayer-based systems

Polyelectrolyte multilayers are another method investigated for on-demand release coatings. Polyelectrolytes (polymer + electrolyte) consisting of the fraction of monomeric units with ionized functional groups (cationic/anionic polyelectrolytes) can be assembled on the surface of nanoparticles via an LbL approach. Coating with several functionalities can be created with the stepwise electrostatic assembly LbL deposition procedure involving oppositely charged surface species. Charged molecular or supramolecular building blocks can be assimilated into the layered architecture. The encapsulated inhibitors will be released in a regulated manner when the confirmation of the polyelectrolyte molecules changes due to

fluctuations in pH. A number of works are available on the topic where more details can be found (Biesalski et al., 2002; Zheludkevich et al., 2007; Shchukin & M3hwald, 2007a; Grigoriev et al., 2009; Skorb et al., 2009; Andreeva et al., 2010; Wei et al., 2015; Figueira et al., 2016; Stankiewicz & Barker, 2016; Dewald & Fery, 2017).

2.3 Organic-inorganic structures

Organic-inorganic hybrid materials have attracted significant research attention for their potential applications in various fields including nanomachines (Lee et al., 2009), sensors (Coe et al., 2002), catalysts (Saparov & Mitzi, 2016), and energy materials (Bera & Halder, 2016). These compounds are expected to exhibit additional and novel properties in addition to the intrinsic properties found in the parent materials (G3mez-Romero & Sanchez, 2005). Because of the binding strength of the supramolecular interactions, the metal-to-ligand interaction is a favorite that can offer a large diversity in thermodynamic stability and kinetic lability (Schubert & Eschbaumer, 2002; Beck et al., 2005). The bond energies of the resulting structures can display a wide variation, from very weak to energies close to that of covalent bonds (Wilkins, 2003). The properties of these compounds can be finely tuned through the proper selection of the metal and the ligands.

Among these MOFs [crystalline porous hybrid materials containing metal ions/metal-oxo units coordinated by electron (e^-)-donating organic ligands] are a comparatively new class of nanoporous materials that have shown great potential in different application areas such as gas storage and separation, energy storage and conversion, sensing, catalysis, drug delivery and imaging, and corrosion inhibition (Yaghi et al., 1995; Morozan & Jaouen, 2012; Choi et al., 2015; Kumar et al., 2017a,b). Some works on MOFs utilizing host-guest concepts (Li et al., 2009) and various 2D and 3D supramolecular assemblies (He et al., 2011; Zhang et al., 2013; Tian et al., 2014; Tian et al., 2016) are available. Dopamine grafted MOFs (Wang et al., 2017b), binary linear saturated carboxylates of Zn (Mesbah et al., 2011), Co-, Ni-, and Cu-based MOFs (Kumaraguru et al., 2017), etc., have been reported in anticorrosion coating applications. They can effortlessly form MOF-polymer/inorganic composite anticorrosion coatings.

Wang et al. reported a novel environmentally friendly dopamine (DA)-MOFs possessing a distinct structure with adjustable pore size, where DA was grafted on the MOF exterior surface. DA-MOF structures were confirmed by FTIR, TG, and N_2 adsorption tests. The synthesis technique employed was found to be helpful in improving their

dispersion in the waterborne epoxy resin and the coating cross-linking density. Salt spray tests conducted on coated carbon steel with pure epoxy, epoxy containing 0.3, 0.5, 0.7, 1.0, and 2.0 wt.% DA-MOFs, showed that serious rusting occurred for the pure epoxy resin, whereas little rust/pitting with no blistering was observed for a 0.5 wt.% DA-MOF coating, indicating enhanced barrier properties. EIS studies showed resistance values $>3.18 \times 10^8 \Omega \text{ cm}^2$ for the coating with optimum DA content. The results also demonstrated that when the DA filler was too little, the protection offered was not good; conversely, when the filler content was high, they aggregate and badly affected the coating performance (Wang et al., 2017b).

Kumaraguru et al. synthesized Co, Ni, and Cu MOFs based on the trimesic acid ligand. Field emission SEM images showed that Ni-MOF, Cu-MOF, and Co-MOF, respectively, showed 1D nanorod, macroporous foam-like, and large chunky particle morphologies. EIS studies of MOF pigment-incorporated paint-coated mild steel in 3.5% NaCl and 0.1 N HCl showed that the corrosion prevention capability of the coating was in the order Ni-MOF > Co-MOF > Cu-MOF, and the variation was attributed to the difference in morphologies. The lower corrosion resistance property of Cu-MOF was associated with the porous foam morphology in which the NaCl and HCl solution effortlessly penetrates through the pores. The nanorod morphology and compact packing of the Ni-MOF were suggested to be beneficial. Adhesion experiments showed that epoxy coating with optimum DA-MOFs improved the coating adhesion considerably (Kumaraguru et al., 2017).

Mesbah et al. reported Zn-based MOFs, the binary Zn-carboxylates $\text{ZnC}_n\text{C}_{n'}$ [C_n and $\text{C}_{n'} = \text{CH}_3(\text{CH}_2)_{n-2}\text{COO}^-$] which were employed as corrosion-protective coatings on electrogalvanized steel as a replacement for phosphating treatments in automotive processes (Mesbah et al., 2011). Zhang et al. employed a simple ligand-assisted conversion approach to transform ZnAl-CO_3 LDH precursor buffer layers to well-intergrown zeolitic imidazolate framework (ZIF-8) coatings on Al. Electrochemical polarization studies showed that the ZIF-8-coated Al showed corrosion current densities ~ 4 orders of magnitude inferior to that of bare Al. The improved performance was attributed to the inherent hydrophobicity and water stability of ZIF-8 as well as to the uniform and well-intergrown microstructures (Zhang et al., 2018b).

The supramolecular chemistry of phosphonate ligands has high importance in corrosion research. Demadis et al. have provided a detailed account of metal phosphonate anticorrosion coatings (Demadis et al., 2012). Zang et al. reported two alkaline earth metal phosphonates $[\text{M}(4\text{-cppH}_2)_2]$, where M corresponds to Sr or

Ba (for compounds 1 and 2) and 4-cppH_3 corresponds to 4-carboxylphenylphosphonic acid. Compound 1 has a chain structure made up of edge-sharing $\{\text{SrO}_8\}$ polyhedra and $\{\text{PO}_3\text{C}\}$ tetrahedra, whereas the edge-sharing $\{\text{BaO}_8\}$ polyhedra were linked by the $\{\text{PO}_3\text{C}\}$ tetrahedra to form a 2D inorganic layer in compound 2. Adjacent chains in compound 1 or layers in compound 2 were cross-linked by H bonds, creating 3D supramolecular assemblies. Corrosion studies on the metal phosphonate-coated Mg alloys showed that both compounds 1 and 2 presented considerably enhanced anticorrosion behavior when compared to the bare substrate (Zang et al., 2011). Several hydrophobic and water-stable MOFs reported in the literature have the potential for application in corrosion prevention coatings (Loiseau et al., 2004; Park et al., 2006; Cavka et al., 2008; Marmisollé et al., 2015).

Organosilicon-based structures are explored for developing self-cleaning hydrophobic surfaces (Feher et al., 1989; Loy & Shea, 1995). Maji and Halder in a recent work described the design and assembly of a novel self-cleaning, hydrophobic, pollution-protective coating comprising polyhedral oligomeric silsesquioxane (POSS) and diphenylalanine. The coating was found to be multipurpose and was effective against corrosion and bacterial attack. The POSS improved the hardness, stability, and thermo-compatibility, whereas the diphenylalanine motif controlled the self-assembly and exhibited distinctive hydrophobicity. The hybrid building blocks self-assembled non-covalently in an antiparallel way to form a supramolecular layer-like structure with better roughness (Maji & Halder, 2017). Longhi et al. reported that the integration of POSS enhanced the barrier properties of the epoxy coating, due to the greater cross-linking that happened between the resin and the POSS. Three POSSs (glycidylisobutyl, triglycidylisobutyl, and glycidyl-POSSs) were studied with epoxy resin, and the authors observed the best corrosion resistance properties with the glycidylisobutyl-POSS-epoxy-coated sample (Longhi et al., 2017). More details on MOFs are provided in § 3 and § 4.

2.4 Others

A few interesting works are available on dendrimer-based (Crooks et al., 2001; Zimmerman & Lawless, 2001) and graphene-based coatings (Zu & Han, 2009), where supramolecular interactions are utilized. Graphene-based corrosion-preventive and self-healing coatings can be attractive as they have several advantages such as low cost, thermal/chemical stability, environmental

friendliness, and high thermal/electrical conductivity. Non-covalent functionalization of graphene can be successfully achieved to promote the process of molecule-assisted self-assembly to form supramolecular structures (Ren et al., 2010; Kuila et al., 2012; Tang & Zhou, 2013). More details on the supramolecular approaches to graphene can be found in following references (Chen et al., 2008; Hsieh et al., 2014; Dwivedi et al., 2015; Ciesielski & Samorì, 2016; Lu et al., 2017; Nguyen et al., 2017; Xu et al., 2018).

Xu et al. reported a novel poly(urea-urethane)-graphitic carbon nitride nanosheet (PUU-g-C₃N₄ NS) composite, where the multiple H bonds within the PUU matrix were found to be helpful in providing self-healing properties, whereas the g-C₃N₄ NS cross-linkers considerably enhanced the mechanical properties. The anticorrosion performance and the self-healing capacity of the PUU-g-C₃N₄ NS-coated (by the drop-casting method) 2024 Al alloy were evaluated by EIS, laser microscopy, and scanning Kelvin probe method. The results of the study showed that the PUU-g-C₃N₄ NS coating retained its protective ability even after 20 days of immersion in 0.5 M NaCl. The self-healing studies performed on the coated surface showed that an intentional scratch vanished and the anticorrosion capability regenerated within 10 min. The introduction of g-C₃N₄ NS was found to be beneficial for the composite material and enhanced the anticorrosion barrier property/anti-penetration ability and retained reasonable self-healing property under high-humidity circumstances (Xu et al., 2018).

The above studies clearly showed that supramolecular interactions are mainly utilized in surface-coating applications to develop advanced coatings with multifunctionalities such as self-healing capability. Many approaches were investigated in this direction, and each of them has its own merits and demerits. More studies in this direction are demanding and can indeed lead to novel commercially relevant coating technologies. The potentials of future developments are discussed in § 5.

3 Corrosion inhibitors

The application of corrosion inhibitors is one of the best methods of controlling the corrosion of metallic structures, and it is widely used in industries around the world such as the oil and gas sectors, the water treatment plants, and the paints and coatings industries. A significant extent of research and development has been performed in developing corrosion inhibitors for various systems depending on the medium treated, the type of metal used, and the

type of corrosion encountered (Nathan, 1973; Sastri, 1998; Shibli & Saji, 2005; Saji, 2010). In various industrial applications, corrosion inhibitors are used in combination with other additives such as antiscalants and biocides.

Supramolecular compounds and concepts have been widely researched to develop novel and more efficient corrosion inhibitor systems. A number of recent reports on organic and polymeric corrosion inhibitors where supramolecular concepts have been utilized are available.

3.1 Polymeric inhibitors

Polymers are considered economical and efficient corrosion inhibitors due to their large surface area and inherent stability. One main advantage of using polymers is that they can easily form complex supramolecular structures with the different functional groups attached to the polymer backbone with cations/metal ions, as well as a large area complex network at the surface. The inhibitive power of polymers is associated with the existence of cyclic rings with π e⁻ and heteroatoms, which are the chief adsorption sites (Umoren et al., 2006, 2008; Baskar et al., 2014; Umoren & Solomon, 2014; Tiu & Advincula, 2015; Kumar et al., 2017a,b).

Different types of polymers including synthetic polymers, conducting polymers, natural polymers, and coordination polymers have been investigated as corrosion inhibitors. Literature analysis suggested that water-soluble thermoplastic polymers exhibited noteworthy corrosion inhibition at low concentrations in aggressive media, especially in acidic media (Chetouani et al., 2004; Manivel & Venkatachari, 2007; Amin et al., 2009; Srivastava et al., 2010). Studies on conducting polymers conversely displayed comparatively low inhibition efficiency, which was attributed to their brittle nature and poor film-forming ability (Jianguo et al., 1995; Prakash et al., 2008). Several recent reviews are available on polymeric corrosion inhibitors, where more details can be found (Umoren, 2009; Arthur et al., 2013; Umoren & Solomon, 2014; Sabirneeza et al., 2015; Tiu & Advincula, 2015; Umoren & Eduok, 2016).

Most of the recent works reported on natural and synthetic supramolecular polymeric corrosion inhibitors focused on CDs (see § 3.1.1) and PUs (see § 3.1.2), respectively.

3.1.1 Natural polymers

Several naturally occurring polymers such as chitosan, pectin, starch, gum Arabic, gellan gum, and cellulose

derivatives have shown promising results as metallic corrosion inhibitors in various corrosive environments (Umoren & Solomon, 2014). Umorean et al. have reviewed carbohydrate polymers as corrosion inhibitors. The authors classified the carbohydrate polymers into exudate gums, carboxymethyl and hydroxyethyl cellulose, starch, pectin, pectate, chitosan, carrageenan, alginate, dextrin, and CD (Umoren & Eduok, 2016). Considering the supramolecular principles, the most important candidate to be discussed in this category is perhaps the CDs.

3.1.1.1 CDs

Reports on short-chain dextrans and CDs as corrosion inhibitors are available since the 1970s (Shibad & Balachandra, 1976; Talati & Modi, 1976). Literature analysis revealed that many recent works on CDs utilized the host-guest chemistry where CD-inhibitor supramolecular complexes were employed to achieve a steady and slow release of inhibitors. The most widely investigated CD is the β -CD due to its low cost and favorable properties (see Figure 4 and Table 1) (Szejtli, 1998; Uekama et al., 1998; Chernykh & Brichkin, 2010).

Fan et al. has investigated the corrosion inhibition properties of β -CD and octadecylamine (ODA) complexes prepared by the grinding method (Fan et al., 2014a) and the speeding hybrid method (Fan et al., 2014b). $^1\text{H-NMR}$

studies proved that a supramolecular host-guest complex was formed and was expected to function by releasing ODA molecules in the boiler condensate water, forming a hydrophobic surface layer on the steel (Fan et al., 2014a,b). The XRD and SEM results clearly showed its protection effect (Figure 5). When the bare sample revealed severe uniform corrosion with the corresponding appearance of rust phases in the XRD (Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$), the sample immersed in the 50 mg l^{-1} inhibitor solution does not show XRD peaks corresponding to rust, and the surface remained smooth without a corrosive attack (Figure 5). Both the anodic and the cathodic curves were shifted in the presence of the inhibitor, indicating a mixed-type mechanism. The polarization and Nyquist plots (Figure 5) showed a continuous increment of inhibition efficiency with the dosage. The capacitive behavior in the EIS and the mixed inhibition by polarization suggested that the inhibitor works by effective surface adsorption (Fan et al., 2014b).

In a more recent report, the authors reported a host-guest supramolecular complex (HPDA) comprising of 2-hydroxypropyl- β -CD (host) and ODA (guest) as inhibitors. Phase solubility simulation and molecular mechanics calculations showed that HPDA was reasonably stable in water with an apparent association constant value of 9199 mol^{-1} , and its four possible configurations were

Figure 5: XRD and SEM studies of carbon steel without (A, C) and with (B, D) inhibitor addition in condensate water. (E) Polarization curves and (F) EIS plots recorded as a function of inhibitor concentration ($40 \pm 5^\circ\text{C}$, $\text{pH } 5.68 \pm 5$) (reproduced with permission from Fan et al., 2014b; Copyright @ Elsevier).

proposed to co-exist in solution. Weight loss studies disclosed that the inhibition efficiency of HPDA was concentration and temperature dependent. A maximum efficiency of 92.6% was achieved with a 50 mg l⁻¹ inhibitor concentration at 40°C. The inhibition mechanism was found to be mixed with predominant anodic inhibition. Adsorption experiments showed that the inhibition mechanism involves chemisorption and obeying the Langmuir model. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy studies suggested that the chemisorption has resulted from the self-assembly of the guest molecules with a tilted orientation (Fan et al., 2014a).

Well acidizing procedure in the oil and gas sectors (acids are injected under high pressure through the borehole, where they react chemically and dissolve the rocks) demands extreme care in the corrosion protection of tubular materials and other equipment employed (Finšgar & Jackson, 2014). Zou et al. prepared β -CD-organic phosphoric acid [2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA)] supramolecule and investigated for acid-rock reaction. The supramolecular compound had the lowest corrosion rate when compared to the mud acid and PBTCA systems. The corrosion rate of the mud acid was 17.2% in 15 min, while the corresponding rates of the PBTCA and β -CD-PBTCA were 7.3% and 4.8%, respectively. The reason for the β -CD-PBTCA having the lowermost rate was suggested to be the host-guest chemistry, where the host releases PBTCA guests slowly and steadily (Zou et al., 2011). Wei et al. patented a corrosion inhibitor combination that comprise of 30–70 (wt. parts) CD derivative, 10–50 organic azole compound (e.g. BZT), 5–20 inducer, and 6–60 H₂O. The ultra-fine grinding preparation method used to fabricate the title product involved the following steps: mixing the CD derivative and H₂O, transferring the paste to a dispersion grinding machine, grinding at 500–1000 r min⁻¹, adding the BZT, continuously grinding for 10–30 min, slowly dropping the inducer, grinding at 2000–5000 r min⁻¹ for 30–60 min, and vacuum drying at 60–80°C. With an inhibitor concentration of 20–50 mg l⁻¹, >90% corrosion inhibition efficiency was achieved for Cu and its alloys in the cooling water systems (Wei et al., 2014a).

Polymer flooding is an effective method to improve the oil yield in chemically enhanced oil recovery, and polyacrylamide (PAM)-based polymers were primarily used for this purpose (Smets & Hesbain, 1959; Muggeridge et al., 2013). β -CD-incorporated PAM supramolecular polymers have been shown to be superior for oil recovery [216]. In this direction, He et al. reported a supramolecular polymer [poly(AA-AM-AMPS-MAH- β -CD)] containing β -CDs as corrosion inhibitors for carbon steel in 0.5 M HCl,

where AA, AM, AMPS, and MAH, respectively stands for acrylic acid, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and maleic anhydride grafted polymers. Their electrochemical studies suggested that the supramolecular polymer was a mixed-type inhibitor, and the effective surface adsorption offered the protection via coordinate covalent bond formation through e⁻ pairs of N, O, and S heteroatoms in the polymer. The inhibition efficiency was found to be directly related to the polymer concentration (He et al., 2014).

3.1.1.2 Calixarenes

Calixarenes are macrocyclic compounds made up of phenolic units connected by methylene bridges and are attractive building blocks for the realization of supramolecular polymers. They can be present in many conformations such as cone, partial cone, 1,2-alternate, and 1,3-alternate. The chance to functionalize the calixarene dais at the upper and lower rims permits embedding of multiple self-assembly motifs on the same molecule (Zhang et al., 1996; Vicens & Harrowfield, 2007; Dalcanele & Pinalli, 2013).

Benabdellah et al. have shown that two novel calixarenes, 1,3,5-tri-carboxy 2,4,6-trimethoxy dinitro calix[6]arene and 1,3,5-tri (2-ethyl imidazole acetamide) 2,4,6-trimethoxy calix[6]arene, offer potential as mild steel corrosion inhibitors (Benabdellah et al., 2007). Kaddouri et al. have synthesized four calixarenes comprising one to four 4-imidazolethylamidocarbonyl groups, and inhibition efficiencies at the range of 94–100% were obtained at 10⁻⁴ M concentration of the optimum inhibitor (mild steel, 1 M HCl). The inhibition efficiency was found to have a direct relation with the number of 4-imidazolethylamidocarbonyl groups attached to the calixarene backbone (Kaddouri et al., 2008). Their subsequent works reported an efficiency as high as 98%, and the protection has a direct dependence on the inhibitor concentration and was temperature independent. Polarization studies have shown that the calixarenes are mixed-type inhibitors. Adsorption obeyed the Langmuir isotherm (Kaddouri et al., 2013).

3.1.2 Synthetic polymers

As discussed in the previous section, synthetic polymers having polar functional groups have attracted significant research attention as metal corrosion inhibitors (Jianguo et al., 1995; Abd El-Ghaffar et al., 1998; Umoren et al., 2006). When considering the possible supramolecular architecture, the major polymer to be mentioned in this category is conceivably PUs. PUs have a wide range of

applications in coatings, adhesives, packaging materials, and biomedical aids (Thomson, 2005; Mishra et al., 2010). Suitable chemical modification of PUs can make it water soluble and electrically conducting (Williams et al., 2008; Banerjee et al., 2011a). The ionic centers of a PU ionomer can be hydrated with water, which can result in supramolecular assemblies (Dieterich, 1995). Also, the self-organization potential of block polymers is expected to make supramolecular assemblies (Žigon & Ambrožič, 2003). The following section discusses works reported on PU-based corrosion inhibitors.

Banerjee et al. have investigated aliphatic PU-based inhibitors (Banerjee et al., 2011a,b). Several PU ionomers with various degrees of sulfonation (DSs) [diphenyl methane diisocyanate-based sulfonated PUs (SPUs)] were studied as corrosion inhibitors (mild steel, 0.5 M H_2SO_4). Nucleophilic substitution reaction in which the urethane hydrogen was removed by reacting PU and NaH at $-5^\circ C$, followed by a reaction with propane sultone, was used for the preparation. An inhibition efficiency $>90\%$ was achieved with a very low concentration (20 ppm) of the SPU. Both the weight loss and potentiodynamic polarization studies showed that the corrosion rates decreased as the concentration and DS increased. Potentiodynamic polarization studies (Figure 6) showed a mixed-type inhibitor mechanism. The addition of SPU shifted the E_{corr} slightly toward negative values (~ 30 mV)

and reduced both the anodic and the cathodic current densities significantly. Inhibition efficiency followed an initial rapid increase and reached a maximum value of 100 ppm (Figure 6). No significant increase in efficiency was observed for >100 ppm of SPU, which was accredited to the saturation of the adsorption process, whereas the increase in efficiency with DS was attributed to the enhanced absorbability due to the increase in the number of active centers (ionic sulfonate group). The AFM images revealed that the deposition of the polymer layer caused surface smoothening (Figure 6). Average roughness factors calculated with different inhibitor addition were found to be 127, 78, and 52 nm for SPU-88 (5 ppm of inhibitor), SPU-48 (60 ppm), and SPU-88 (60 ppm), correspondingly. The inhibition efficiency was also predicted theoretically by quantum chemical calculations. For the pure PU unit, the e^- density of the highest occupied molecular orbital (HOMO) was localized mostly on two benzenes with lesser contribution from the diisocyanate, while for the sulfonated polymer, the e^- density of the HOMO was localized chiefly on the sulfonate group, indicating that the bonding of the sulfonated inhibitor unit with vacant d-orbital of metals can be more facile when compared to bonding through the benzene ring. The decrease in HOMO-lowest unoccupied molecular orbital (LUMO) energy gap with an increase in DS suggested that the reactivity of the inhibitor molecule for surface

Figure 6: (Left) Scheme showing the evolution of lower- and higher-molecular-weight species during sulfonation. (Right) Potentiodynamic polarization plots (A) and inhibition efficiency as a function of inhibitor concentration and DS (B). AFM micrographs of steel after electrochemical measurement at different concentrations: (A) 5 ppm SPU-88, (B) 60 ppm SPU-88, and (C) 60 ppm SPU-48 (reproduced with permission from Banerjee et al., 2011b; Copyright © The Royal Society of Chemistry).

adsorption increased with increasing DS [229]. In a related publication, the authors reported a 95% efficiency for 100 ppm hexamethylene diisocyanate-based aliphatic PU for mild steel in acidic pH (Banerjee et al., 2011a).

Kumar et al. synthesized two PU-based tri-block copolymers, namely, poly(N-isopropylacrylamide)-*b*-polyurethane-*b*-poly(N-isopropylacrylamide) (PIA-PU-PIA) and poly(tert-butylacrylate)-*b*-polyurethane-*b*-poly(tert-butylacrylate) (PtBA-PU-PtBA), by atom transfer radical polymerization (ATRP) and employed them as inhibitors for mild steel. Results of electrochemical studies revealed that the polymers are mixed-type inhibitors with a predominant cathodic inhibition (mild steel, 0.5 M H₂SO₄), with efficiency as high as 99% at 1600 ppm and was found to increase with the increase in the inhibitor concentration. Competitive physisorption and chemisorption were suggested as the adsorption mechanisms. The adsorption of PIA-PU-PIA on steel obeyed the Langmuir adsorption isotherm, while that of PtBA-PU-PtBA obeyed the El-Awady isotherm. Quantum chemical calculations showed that the relative strength of the inhibitor action depends on the tendency of the polymers for e⁻ donation and also on the polymer molar volume (Kumar et al., 2017). Yang et al. synthesized novel trianiline containing water-soluble PUs by polymerization of polyethylene glycol, toluene diisocyanate, and amine-capped aniline trimer and achieved 97% efficiency at 200 mg l⁻¹ (mild steel, 1 M HCl) (Yang et al., 2017).

3.2 Metal-organic structures

Here, recent works on inorganic-organic hybrid corrosion inhibitors are presented. The section is presented under three subheads, namely, coordination polymers, MOFs, and metal-organic phosphonates, even though the criteria of classification are not impeccable. Metal phosphonates are discussed separately as there a large number of works reported in this area.

3.2.1 Coordination polymers

Many works reported in this category employed Schiff base (compounds made by the condensation of amino and carbonyl compounds) monomers/polymer-complexes as acid corrosion inhibitors (Desai et al., 1986; Achary et al., 2007; Hosseini et al., 2007; Şafak et al., 2012; Saha et al., 2015). The presence of both hard N and O and soft S donor atoms in the ligands helps them to coordinate with a wide range of transition metal ions

straight away, yielding stable and deeply colored metal complexes. A recent review is available on the coordination chemistry of supramolecular Schiff base polymer complexes, where more details on their synthesis, structure, and characterization are described (El-Bindary et al., 2016).

Das et al. prepared three ligands, namely, L¹ [N,N-dimethyl-N'-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine], L² [2-morpholino-N-(1-(pyridin-2-yl)ethylidene)ethanamine], and L³ [(2-(piperidin-1-yl)-N-(1-(pyridin-2-yl)ethylidene)ethanamine)], that were used to make five Cd(II) Schiff base complexes: [Cd(L¹)₂](ClO₄)₂, [Cd(L¹)(Cyanoacetate)(OAc)], [Cd₂(L¹)₂(N₃)₄], [Cd(L²)(N₃)₂]_n, and [Cd₂(L³)₂(N₃)₄]_n (Figure 7). Their acid corrosion inhibition for mild steel has been examined in 15% HCl. Representative structures of coordination polymer unit and the supramolecular network of complexes 3 and 4 are provided in Figure 7. Complex 3 was a symmetric dimeric compound crystallized in the space group of P2₁/n, where each Cd²⁺ ion was located in an octahedral geometric environment. The octahedral geometry of each Cd(II) ion was satisfied by one tridentate Schiff base ligand (L¹), one terminal azido ion, and two bridging azido ions. Two bridging azido ions create a bridge between the two Cd(II) centers through a μ-1,1 double-bridged end-on fashion. Each dimeric unit linked with each other via C4–H4...N3 hydrogen bonding, resulting in a 1D chain-like structure along the *c* axis. Complex 4 forms a 1D coordination polymeric zigzag chain along the *c* axis (Figure 7). Each Cd atom was coordinated by three N donors (in distorted octahedral fashion) from a tridentate chelating Schiff base ligand (L²), one terminal azido ion, and two N donors from two bridging (crystallographically different) azido ligands. These two azido ligands were accountable to make this coordination polymer, creating a bridge between two crystallographically same Cd centers via a μ-1,3 end-end fashion. Two such 1D coordination polymeric chains are further connected via C2–H2...O1 hydrogen bonding to create a 2D sheet-like structure (Figure 7). The polarization curves showed improved corrosion protection by the inhibitors, and the variation was suggested to be due to a mixed inhibitor mechanism. Nyquist plots showed a depressed semicircle in the frequency range of 0.1–10 mHz, whose shape and size progressively augmented with the inhibitor addition up to 0.1 g l⁻¹, with the associated enhancement in charge transfer resistance (*R*_{ct}) (Das et al., 2017).

Liu et al. synthesized a Cu coordination polymer, [Cu(C₆H₄N₃)]_n, incorporating a corrosion inhibitor (BTA) through the hydrothermal reaction of Cu(NO₃)₂, 1H-BTA, and NH₃. The asymmetric unit contained two BTA ligands

Figure 7: (A) Scheme showing synthesis procedure of Cd(II) complexes 1–5. (B) Dimeric unit structure and supramolecular network structure of complex 3. (C) Coordination polymeric structure and the 2D supramolecular network of complex 4 (reproduced with permission from Das et al., 2017; Copyright @ The Royal Society of Chemistry).

and three crystallographically different Cu(I) cations. Two of the Cu(I) cations (with linear two and four coordinated tetrahedral geometries) were positioned on sites with crystallographically imposed two-fold symmetry. The third Cu(I) cation (planar three coordinated geometry) was in a general position. Two Cu(I) cations were doubly bridged by two BTA[−] ligands to give a non-centrosymmetric planar [Cu₂(BTA)₂] subunit, and the two such subunits were arranged in an antiparallel means to form a centrosymmetric [Cu₂(BTA)₂]₂ building unit. These units are linked in a crosswise style via the sharing of four coordinated Cu(I) cations, Cu–N bonding, and bridging by two coordinate Cu(I) cations, resulting in a 1D chain along the *c* axis. The 1D chains were further connected by C–H⋯ π and van der Waals interactions to form a 3D supramolecular architecture (Liu et al., 2014).

Heterocyclic aromatic compounds (e.g. azoles) have been shown to be supreme Cu corrosion inhibitors. Recent works explored coordination networks of heterocyclic aromatic compounds as corrosion inhibitors (Fernando et al., 2010, 2012). Fernando et al. have studied the effects of Zn, Cd, Ag, Na, and NH₄⁺ on the structurally adaptable 3D layered supramolecular frameworks for Cu corrosion inhibition. Five compounds based on pyrazole-4-sulfonate anion (L[−]) (Figure 8A) were synthesized by the reaction of pyrazole-4-sulfonic acid (HL) with ZnO,

CdCO₃, Ag₂O, NaOH, and NH₃, and the resulting Zn(4-SO₃-pzH)₂(H₂O)₂, Cd(4-SO₃-pzH)₂(H₂O)₂, Ag(4-SO₃-pzH), Na(4-SO₃-pzH)(H₂O), and NH₄(4-SO₃-pzH) were studied by single crystal XRD, infrared (IR), NMR, and TGA and explored as Cu corrosion inhibitors. As a representative example, the alternating inorganic-organic layered structure for ZnL₂(H₂O)₂ is provided. The thermal ellipsoid design (50% probability) of ZnL₂(H₂O)₂ displaying the coordination sphere around Zn is also shown (Figure 8B). The inorganic layer (Figure 8C) is composed of a rectangular pattern of Zn²⁺ ions, each coordinated by two SO₃[−] and two H₂O molecules. The H₂O molecules form an H bond with a sulfonate group from an adjacent unit, and a bifurcated H bond with two sulfonate groups, one bound to the same Zn²⁺ and the other from a different neighboring unit. Within the organic layer, the pyrazole moieties were structured in infinite π -stacked columns. The larger Ag⁺ and NH₄⁺ form anhydrous complexes, while complexes of smaller Zn²⁺, Cd²⁺, and Na⁺ comprised one or two H₂O molecules per “metal-L” unit. Noteworthy corrosion protection was obtained with all these compounds at pH 4 and 3. At pH 3, corrosion rates at the range of 0.04–0.05 mm year^{−1} was obtained, while at pH 4, corrosion rates were at the range of 0.02–0.04 (corrosion rates of control samples were 0.31 and 0.11 mm year^{−1} at pH 3 and 4, respectively) (Fernando et al., 2012).

Figure 8: (A) Multiple binding modes of ligand L^- (pyrazole-4-sulfonate anion). (B) Thermal ellipsoid design (50% probability) of $\text{ZnL}_2(\text{H}_2\text{O})_2$ displaying the coordination sphere around Zn. (C) Alternating inorganic-organic layered structure of $\text{ZnL}_2(\text{H}_2\text{O})_2$ (reproduced with permission from Fernando et al., 2012; Copyright @ The Royal Society of Chemistry).

3.2.2 MOFs

MOFs are often called coordination polymers; however, it differs from usual coordination polymers (Biradha et al., 2009; Batten et al., 2012) and exhibits higher thermal stability, permanent porosity, and structural durability (Silva et al., 2015). MOFs comprising metal-ligand complexes, continuous 2D/3D structure, π e^- -rich topologies, and hetero-aromatic components are prospective materials for corrosion inhibitors (Massoud et al., 2009; Etaiw et al., 2011; Morozan & Jaouen, 2012) due to their high surface area, supramolecular nature, and unique topologies. Morozan and Jaouen (Morozan & Jaouen, 2012) and Silva et al. (Silva et al., 2015) have briefed MOFs-based corrosion inhibitors in their reviews. The following sections describe interesting recent reports.

Etaiw et al. synthesized $[\text{Ag}(\text{qox})(4\text{-hb})]$ (monoclinic, space group $P2_1/c$) by self-assembly reaction between AgNO_3 and quinoxaline (qox) in the presence of 4-hydroxybenzoate (4-hb) in water/acetonitrile solvent. Each Ag atom in the discrete binuclear array was coordinated to the N atom of qox and two O atoms of two 4-hb ligands forming an eight-atomic distorted polygon. The network structure of the MOF was built by a vast number of distinct binuclear molecules that extend along the a axis to form a 2D array via H bonds (3.225–3.262 Å) and π - π stacking (3.046–3.222 Å). The wide-ranging H bonds

(2.524–3.003 Å) and π - π stacking (2.841–3.287 Å) link the 2D arrays, creating a 3D network. The corrosion inhibition efficiency of the prepared MOF for carbon steel was studied in 1 M HCl. The inhibitor suppressed both the cathodic and the anodic processes (β_a and β_c), suggesting a mixed mechanism. The adsorption obeyed the Langmuir isotherm, and the adsorption free energy showed a simultaneous physical and chemical adsorption, which was assumed to be due to the adsorbed neutral molecules via e^- sharing between the N and O atoms of the inhibitor molecule and the metal surface. Adsorption can also happen via π e^- interactions within the MOF ring structure (Etaiw et al., 2013). The authors recently reported $[\text{Cd}(\text{SCN})_2(6\text{-mqin})_2]$, which was obtained by the reaction of $\text{CdSO}_4 \cdot 5\text{H}_2\text{O}$ with 6-methylequinoline (6-mqin) as inhibitors for Cu in 1 M HCl (Etaiw et al., 2017).

Beltran et al. synthesized a series of tin-phthalocyanines and employed as inhibitors (carbon steel, H_2S saturated brine). The authors suggested that as the intermolecular interactions modified the aliphatic backbone conformations and induced various kinds of deformation in the phthalocyanine ligands, they can have a noteworthy influence on the molecular packing and in turn can affect the inhibition efficiency. The supramolecular links of the crystallographic lattices comprise π - π , σ - π , $\text{N}_{\text{azo}} \cdots \text{H}-\text{C}_{\text{ar}}$, $\text{O}-\text{C}=\text{O} \cdots \text{H}-\text{C}_{\text{ar}}$, and $\text{O}=\text{C}-\text{O} \cdots \text{H}-\text{C}_{\text{ar}}$ interactions. The best inhibitor efficiency (~88%) achieved was

credited to the parallel-oriented chemisorption of the nanocap metal complexes at the metal surface (Beltrán et al., 2005).

3.2.3 Metal-organic phosphonates

Phosphonate ligands have attracted considerable basic and applied research attention. They have been extensively used in various technological applications including water treatment, oilfield drilling, and corrosion control. In aqueous solutions, water found in their lattice can get involved in extensive H bonding, resulting in supramolecular network formation (Demadis et al., 2012), which was widely used in supramolecular chemistry and crystal engineering (Penicaud et al., 1998; Distler et al., 1999; Serre & Férey, 1999). They have the ability to chelate with metal ions to form supramolecular structures.

The most extensively used organic phosphonic acids include 1-hydroxyethane-1,1-diphosphonic acid, aminotris (methylenephosphonic acid) (AMP), hydroxyphosphonoacetic acid (HPAA), and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC). They are good antiscalants (Dyer et al., 2004).

Organic phosphonates blended with certain metal cations (metal phosphonates) and polymers (metal phosphonate coordination polymers) can reduce the optimal inhibitor concentration and can enhance inhibition efficiency

(Clearfield, 2002; Demadis et al., 2005a,b, 2008a,b; Naimushina et al., 2013; Gholivand et al., 2016; Gupta et al., 2017). Demadis' research group pioneered this area and reported many works on multidimensional MOFs from the self-assembly of phosphonate/sulfonate-based organic linkers and alkaline/alkaline earth/transition metal centers (Demadis et al., 2005a,b, 2006a,b, 2008a,b, 2009, 2010; Papadaki & Demadis, 2009; Fernando et al., 2010, 2012; Clearfield & Demadis, 2011; Colodreno et al., 2013; Moschona et al., 2018). Papadaki and Demadis reviewed metal phosphonate coordination polymeric corrosion inhibitors (Papadaki & Demadis, 2009). The varying corrosion inhibition efficiencies of different organic phosphonates were explained by the structural differences observed with different metal ions, complex formation capability, and thickness/integrity of the surface film formed. For example, a more effective corrosion inhibition observed for a Zn-AMP film (the Zn-AMP complex formation constant is 16.4) when compared to a Ca-PBTC film (the Ca-PBTC complex formation constant is 4.4) was found to be in accordance with the higher complex formation skill of the former (Knepper, 2003).

The synthesis, structural characterization, and corrosion inhibition of polymeric M-HDTMPs [$M = \text{Zn}^{2+}/\text{Ca}^{2+}$ and HDTMP = hexamethylene-diamine-tetrakis(methylenephosphonate)] were reported. The crystal structure of the synthesized Zn-phosphonate showed a 3D coordination polymeric structure where Zn^{2+} was positioned in a distorted octahedral environment made wholly by

Figure 9: (Left, top) Coordination environment of the Zn^{2+} center showing key bond distances (Å) [$\text{O}(10)\text{-Zn-O}(4)$ non-linear angle- 156.03°]. (Bottom) Coordination modes of the tetrakisphosphonate ligand. The aminomethylene parts of the ligand and the Zn^{2+} centers create a “box” of 160 Å capacity. (Right, top) Surface images of carbon steel without (A) and with 1 mM Zn^{2+} /HDTMP synergistic combination (B). SEM images (bottom) showing the unprotected area (left) where the growth of iron oxides is evident and the protected area (right) where a film of Zn-HDTMP has grown (scale bar: 100 μm) (reproduced with permission from Demadis et al., 2005a; Copyright @ The American Chemical Society).

phosphonate oxygens (Figure 9, top). The sixth oxygen ligand for Zn^{2+} originated from a protonated phosphonate oxygen, O(9), and formed an extended interaction [2.622(3) Å] with Zn^{2+} that provides local stabilization due to a robust H bond, O(9)–H(9)···O(3) (1.879 Å). Two Zn^{2+} centers and the aminobismethylenephosphonate parts of HDTMP form an 18-membered ring (Figure 9, bottom), and there is a concentric 8-membered ring made by the same Zn^{2+} and the protonated methylenephosphonate arm involved in the long $\text{Zn}\cdots\text{O}(9)$ interaction. Four phosphonate groups of HDTMP are coordinated to six different Zn^{2+} centers. Their electrochemical corrosion studies with carbon steel showed that a 1:1 combination of Zn^{2+} and HDTMP had excellent inhibition properties (Figure 9). The corrosion rate obtained for a Zn-HDTMP-protected sample by weight loss measurements was $2.11 \text{ mm year}^{-1}$, which was much lesser than that for the control sample ($7.28 \text{ mm year}^{-1}$). The inhibiting film contained Zn^{2+} and P in an approximate 1:4 ratio. The comparison of the SEM images (Figure 9) also demonstrated the improved anticorrosive effect (Demadis et al., 2005a). Papadaki and Demadis provided a detailed account on structures of various metal-organic phosphonates such as $\text{Zn}(\text{AMP})(\text{H}_2\text{O})_3$, $\text{Ca}(\text{PBTC})(\text{H}_2\text{O})_2$, and Ba (or Sr) $(\text{HPAA})(\text{H}_2\text{O})_2$ (Papadaki & Demadis, 2009).

Kending patented soluble polymeric oxidic acids containing Mo, P, W, and/or Si suitable for protection of Al alloys in radiators and cooling systems as on-demand release systems. The oxo anions can be reacted with a metal cation to form a soluble salt, and the salt can be adsorbed on a carrier or sol-gel coating applied on Al or Al alloy surfaces. The resulting adsorbates then become

sparingly soluble and are gradually released in the presence of an aqueous corrosive agent to prevent pitting corrosion. The counterions are preferably selected from Ba, Sr, Al, Zn, or rare earth metals (Kendig, 2003). Studies on adsorption/self-organization of alkylphosphonic acids/phosphoric acid monoalkyl esters on Al showed that the capability for self-assembly is ascribed to the presence of surface reactive groups and long aliphatic/aromatic spacers and can provide a supramolecular order built-up between the spacers (Iris et al., 1998).

3.3 Others

Crown ethers are heterocyclic polyethers that, in their simplest form, are cyclic oligomers of dioxane (Pedersen, 1967; Gokel et al., 2004). They can be considered green corrosion inhibitors. Fouda et al., on their studies on crown ether-based corrosion inhibitors for 430 stainless steels (SSs) in 2 M HCl, observed a linear relationship between protection efficiency and inhibitor concentration. The inhibition efficiency of the studied crown ethers (Figure 10) decreased in the order of (d) > (c) > (b) > (a). The inhibitor adsorption was attributed to the lone pair of e^- of the O and/or N atoms and the delocalized πe^- of the benzene ring, and the difference in the efficiencies of the studied compounds was explained on account of the kind and number of the heteroatoms. The cavities of compounds (a) to (d), respectively contained six O atoms, four O and two N atoms, six O and two N atoms, and eight O atoms. The higher inhibition efficiency of (b) when compared to (a) was attributed to the presence of two N atoms

Figure 10: Crown ethers investigated as corrosion inhibitors. (A) Dibenzo-18-crown-6. (B) 4,13-Diacetyl, 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane. (C) 4,7,13,16,21,24-hexa-oxa-1,10-Diazo-bicyclo-(8,8,8)-hexacosane. (D) Dibenzo-24-crown-8 (reproduced with permission from Fouda et al., 2010; Copyright @ Elsevier).

that can donate e^- and can make a stronger electrostatic interaction with the steel surface. The two alkyl branches in (b) (+I effect) increases the charge density at the N atoms. Despite the presence of the two N atoms in (c), its lower inhibition efficiency when compared to (d) was explained by the higher molecular weight of the latter. The existence of two benzene rings in (d) can make it firm, which can retard the adsorption process. The authors suggested that the presence of more than one orienting groups (O, N) can, in effect, result in better adsorption and, hence, a better corrosion inhibition. Polarization studies suggested a mixed inhibition mechanism. The adsorption followed the Temkin isotherm (Fouda et al., 2010).

Hadisaputra et al. examined the role of the macrocycle ring size on the inhibitive performance of five crown ethers (dibenzo-12-crown-4, dibenzo-15-crown-5, dibenzo-18-crown-6, dibenzo-21-crown-7, and dibenzo-24-crown-8) by the density functional theory. The results showed that dibenzo crown ethers with larger macrocycle ring size have higher HOMO energies than those with smaller macrocycle ring size and hence are more intent to donate e^- . The HOMO energy levels followed the order of DB24C8 > DB21C7 > DB18C6 > DB15C5 > DB12C4 and suggested the highest corrosion inhibitor efficiency for DB24C8 (dibenzo-24-crown-8). The optimized geometries of the five crown ethers showed that the HOMO of the crown ethers matches the aromatic π system of the benzene rings, in which the e^- density accumulates on the π e^- multiple bonds of benzene. The phenyl rings of the dibenzo crown ether can have a higher binding contribution to metal surfaces via delocalization of π e^- (Hadisaputra et al., 2017). *Ab initio* quantum mechanical charge field molecular dynamics simulation studies of DB18C6 showed that their backbone has high flexibility in an aqueous medium, assuming structures considerably diverging from that in ideal gas phases (Canaval et al., 2015).

Dendrimer-based systems (Zimmerman & Lawless, 2001) have recently been investigated as corrosion inhibitors owing to their easy preparation methods, solubility, large surface area, and the presence of electronegative heteroatoms (Verma and Quraishi, 2016; Verma et al., 2016). Verma et al. investigated the inhibition properties of two NH_2 -cored dendrimers (mild steel, 1 M HCl). Their weight loss studies showed a maximum inhibition efficiency of 96.95% at 50 mg l^{-1} concentration. Potentiodynamic polarization plots showed that both cathodic and anodic reactions were affected in the presence of dendrimers, signifying a mixed mechanism. The inhibition efficiency of the dendrimer compounds studied was dependent on their molecular size and the nature of the heteroatoms (O and N). From the HOMO e^- distribution, it was suggested

that the frontier electron density was mostly confined to the center N atom, suggesting that the N atom primarily participated in the e^- donation process (Verma et al., 2016).

Zhang et al. explored the synergistic inhibition properties of polyamidoamine dendrimers with sodium silicate for carbon steel. An inhibition efficiency of ~82% was obtained at relatively low dosages. The mechanism was attributed to chemisorption, which obeyed the Langmuir adsorption isotherm (Zhang et al., 2015).

3.4 Self-assembled monolayers (SAMs)

Many organic compounds have the capability to adsorb spontaneously on a metal surface and form intramolecular or intermolecular SAMs. As discussed in the previous sections, complex polymers can form intramolecular SAMs. The intermolecular SAMs, in general, can form supramolecular structures (Hashim et al., 2010). SAMs can provide a protective hydrophobic barrier hindering ingress of H_2O , O_2 , and e^- to the metal surface (Ramachandran et al., 1996; Adler et al., 2002; Duda et al., 2005). Incorporation of suitable linking agents in the inhibitor can extend the protection. Plenty of information on the SAMs of organic inhibitors is available in the current literature.

Ramachandran et al. explained a SAM model to study the mechanism of action of organic inhibitors such as IMIs. The IMI head group served as a strong Lewis base to displace H_2O from the Lewis acid sites of the Fe-O surface and self-assemble to form an ordered monolayer on the Fe-O surface [$\sqrt{3} \times \sqrt{3}$ for the (001) cleavage surface of α - Fe_2O_3]. The main features of this atomistic model were (i) robust bonding by the IMI head group to the Fe_2O_3 surface; (ii) self-assembly of the head groups to form a dense well-ordered overlayer; (iii) self-assembly of the hydrophobic tails to form a compact closely packed hydrophobic layer; and (iv) sufficient solubility and rate of transport of the inhibitor to the surface, inferring that the SAM can be made quickly before corrosion initiation (Ramachandran et al., 1996).

Alkanethiols and alkyl thiosulfates possess many properties that are beneficial for aqueous self-assembly. It is well known that despite their lower thickness, SAMs of simple aromatic thiols could offer a more efficient protection of Cu surfaces in acidic pH (Lusk & Jennings, 2001; Caprioli et al., 2012). SAMs of longer-chained adsorbates are found to be superior to shorter-chained counterparts owing to their higher van der Waals interactions. IR spectroscopy studies suggested that the eventual breakdown in the protection of *n*-alkanethiol SAMs was attributed to a structural change from a crystalline state to a less densely packed state (Jennings et al., 1998). EIS studies

revealed that SAMs formed from longer-chained thiosulfates showed similar barrier properties to that of thiol-based SAMs when formed in organic solvents but reduced effectiveness when formed in an aqueous solution. However, the water-borne thiosulfate SAMs were found to offer an increase in corrosion resistance by ~2–3 orders of magnitude compared to that of uncoated Cu. Comparison of thiosulfate SAMs with those made from BTA showed that longer-chained thiosulfates could be beneficial in inhibiting Cu corrosion in aqueous environments (Lusk & Jennings, 2001).

Zhang et al. prepared complex SAMs by altering the adsorption of cysteine with dodecylacid and with DAM on Cu surfaces. Electrochemical studies in 0.5 M HCl showed that SAMs suppressed cathodic current densities and shifted the corrosion potential toward a more noble value. A 10 mmol l⁻¹ DAM-modified cysteine/Cu system showed an inhibition efficiency of 90% (Zhang et al., 2010). Scanning tunneling microscopy studies have shown that when mixed SAMs are formed on surfaces with a radius of curvature lesser than 20 nm, they instinctively phase separate in highly ordered phases of unprecedented size. The reason for this supramolecular phenomenon was entirely topological and justified through the hairy ball theorem (Stellacci, 2007).

4 Antibiofouling surfaces

Biofilms grown on metal surfaces pose a big threat to industries worldwide, which can escalate to corrosion and material failure (Almeida et al., 2007; Rao, 2009; Rajasekar et al., 2010; Bixler & Bhushan, 2012; Gupta et al., 2016; Oliva et al., 2017). Table 2 clearly defines the fields susceptible to biofouling (colonization of surfaces by the undesirable buildup of proteins, cells, and organisms), including common examples. In general, medical biofouling (Schulz & Shanov, 2009; Chan & Wong, 2010; Damodaran & Murthy, 2016; Yin et al., 2016) embraces only the biofilm formation, while marine/industrial biofouling (Walker et al., 2000; Fingerman & Nagabhushanam, 2003; Railkin, 2003; Chambers et al., 2006; Cao et al., 2011) embraces a combination of biofilm, macrofouling (by microorganisms), and inorganic fouling. The cause, detection, and control methods vary depending on the nature of biofouling (Table 2). Biofouling can cause pitting corrosion and microbiologically influenced corrosion.

Natural biofouling controls include low-drag and low-adhesion surfaces and surfaces with improved

Table 2: Fields susceptible to biofouling, including common examples (reproduced with permission from Bixler & Bhushan, 2012; Copyright @ The Royal Society Publishing).

Type	Problems
Medical	
Orthopedic implant	Removal owing to infection
Respirator	Ventilator-associated pneumonia
Contact lens	Eye infection
Catheter	Urinary tract infections
Hemodialysis	Infectious break-outs
Teeth/dental implant	Periodontal disease, gingivitis
Biosensor	Failure from fibrous encapsulation
Marine	
Ship hull	Increased fuel consumption
Ship engine	Increased stress from extra drag
Marine platform	Increased marine structure load/stress/fatigue
Metal	Increased biocorrosion
Industrial	
Membrane	Reduced flux
Heat exchanger	Reduced convection efficiency
Fluid flow	Frictional loss in pipes
Drinking water	Pathogens in potable water
Fuel Morton [50]	Diesel fuel contamination
Food, paper, and paint	Food spoilage and worker health risks
Food metal-cutting fluid	Filter blockage and worker health risks

biocompatibility, wettability, and microtexture. For long-term biofouling protection, antifouling coatings coupled with biocides are used (Trojer et al., 2013). An active antibiofouling coating is expected to provide prolonged protection by releasing the incorporated biocides. A number of interesting reports are available on smart on-demand biocide-release coatings (see § 2.2 and 4.2). A few recent reviews are available in this area where readers can get clear fundamentals (Banerjee et al., 2011c; Zhang et al., 2016; Selim et al., 2017).

Banerjee et al. reviewed major approaches in the preparation of antifouling coatings. The authors discussed various strategies relevant to (1) protein antifouling coatings, (2) antimicrobial coatings, and (3) marine antifouling coatings. The protein antifouling coating section has been divided into (i) coatings that resist protein adsorption and (ii) protein-degrading films. Under the first category, poly(ethylene glycol) (PEG)-based coatings were mainly discussed along with SAMs of different compounds with various functional groups including zwitterionic SAMs. Peptide- and peptoid-based protein-resistant surfaces and glycerol/carbohydrate derivatives were also explained. Under the second category, protease-based antifouling films and photoactivated self-cleaning

films were explained comprehensively. Within antimicrobial coatings, two categories were described: (i) coatings that prevent bacterial adhesion and (ii) microbiocidal coatings. The subsections discussed under marine antifouling coatings were (i) amphiphilic antifouling polymer coatings, (ii) enzyme-based antifouling coatings, and (iii) antifouling surfaces with microtopography (Banerjee et al., 2011c).

Selim et al. provided a detailed account of marine foul-release polymeric nanocomposite coatings. They are vibrant non-stick surfaces that prevent surface fouling add-on via physical anti-adhesion terminology. The review classified the fouling-resistant coatings to (i) PEG-based fouling-resistant nanocomposites, (ii) hydrogel-based coatings, (iii) polyzwitterion-based nanocomposites, (iv) hyper-branched nanocomposites, (v) fluoropolymeric coatings, (vi) silicone coatings, (vi) graphene-related materials, and (vii) hydrophobic/superhydrophobic/photo-induced/amphiphilic coatings (Selim et al., 2017).

Good reviews on membrane fouling are available (Zhang et al., 2016). Fabricating antifouling membranes is an important approach to deal with prevalent fouling problems from a variety of foulants and is significant in water desalination processes and industrial wastewater treatment. The authors explained in detail the development of antifouling membranes via surface coating, surface grafting (grafting antifouling materials onto/from membrane surfaces by chemical means), surface bioadhesion, physical blending, and surface segregation (Zhang et al., 2016).

Supramolecular chemistry is considered a rising star in the arena of antibiofouling surface construction (Zhao et al., 2018a). The major objective of this section was to provide a concise overview on the most recent advancements in antibiofouling surfaces and approaches based on supramolecular chemistry, irrespective of the type of biofoulant or application (industrial or biomedical), which are presented under different subheads similar to § 2.

4.1 Block copolymer/gel systems

Polymers are widely used materials for the development of antibiofouling coatings owing to their attractive properties and ease of application (Yang et al., 2014a; Oliva et al., 2017). The antibiofouling polymer coatings mainly exploit three approaches: (i) inhibiting biofouling organisms from surface attachment (fouling-resistant coatings), (ii) decreasing adhesion of biofoulants (fouling release coatings), and (iii) killing of biofoulants (fouling-degrading coatings) (Yang et al., 2014a; Al-Naamani et al., 2017).

Different approaches were put forward to produce innovative antifouling/fouling release coatings that use different polymer chemistries, including usage of self-assembled co-polymers with mesogenic side chains (Krishnan et al., 2006), zwitterionic polymers (Jiang & Cao, 2010), phase-segregated polysiloxane-urethanes (Majumdar et al., 2007), and polymer nanocomposites (Wouters et al., 2010). Good reviews are available where precise details on the types and fundamentals of antibiofouling polymers are explained (Timofeeva & Kleshcheva, 2011; Siedenbiedel & Tiller, 2012; Yang et al., 2014a,b). The following section describes interesting recent reports on supramolecular polymeric surfaces.

It is well known that surface modification by altering the charge or enhancing the hydrophilicity deters a foulant's attachment and adsorption (Combe et al., 1999; Knoell et al., 1999). Hydrophilic PEG-based materials have been extensively employed, as their high degree of hydration upsurges the energetic forfeit of removing water when biofoulants attach, causing resistance to protein adsorption and a foulant's settlement (Krishnan et al., 2008). By careful design and synthesis of the novel additives, it is possible to facilitate control of the assembly process and allow selective surface postmodification in an aqueous environment (Goor et al., 2017a,b). Dankers et al. reported a supramolecular toolbox in this line with various additives (Dankers et al., 2005; Mollet et al., 2014; Pape et al., 2017). By using self-complementary 2-ureido-4[1H]-pyrimidinone (UPy), a modular biomaterial with UPy-modified polycaprolactone (PCLdiUPy) as the basic material was developed firstly (Dankers et al., 2005). In subsequent studies, this scheme has been extended by the amalgamation of PEG2kdiUPy (additive 1) to prevent cell adhesion (Mollet et al., 2014). The authors further extended the supramolecular device with bifunctional PEG10KdiUPy (additive 2) and monofunctional MeOPEG-5KUPy (additive 3) (Figure 11). These additives were designated as they contained larger PEG chains and can lead to more hydrophilic surfaces, leading to less cell adhesion. The additional aliphatic dodecyl spacer (between the UPy and the PEG) can protect the urea groups from interactions with the H₂O of the PEG and can lead to improved anchoring in the PCLdiUPy (Pape et al., 2017). For the pristine PCLdiUPy, the water contact angle was $74.7 \pm 0.2^\circ$. A significant reduction in contact angles was detected with the addition of UPyPEG (UPy-functionalized PEG), with contact angles of $59.8 \pm 1.3^\circ$ for PCLdiUPy with additive 1, $56.7 \pm 0.9^\circ$ with additive 2, and $44 \pm 14^\circ$ with additive 3, reflecting improved hydrophilicity. The cell adhesive behavior was evaluated based on the staining of factin and vinculin. On PCLdiUPy and the mixture with additive 1,

Figure 11: (Left) Chemical structures of the molecules studied. (A) UPy-modified polycaprolactone ($M_n = 2$ kDa). (B) Bifunctional UPy-PEG ($M_n = 2$ kDa). (C) Bifunctional PEG10KdiUPy ($M_n = 10$ kDa). (D) Monofunctional UPyPEG ($M_n = 5$ kDa). (Right) Fluorescence microscopy images of HK-2 cells and HUVECs cultured on spin-coated polymer films for 1 day, stained for F-actin (green), vinculin (red), and nuclei (blue). Scale bar: 100 μm (reproduced with permission from Pape et al., 2017; Copyright @ The American Chemical Society).

HK-2 cells showed a well-spread morphology and clear actin fibers, ending in distinct vinculin spots, indicating good adhesion (Figure 11). Both HK-2 cells and human umbilical vein endothelial cells (HUVECs) showed a clear reduction in adhesion and proliferation on the mixtures with additives 2 and 3 (Figure 11). Remarkably, additives 2 and 3 reduced the cell adhesion, signifying that the chain length of PEG and the better anchoring in the PCLdiUPy base polymer due to the extra alkyl spacer were decisive (Pape et al., 2017).

It is proved that the existence of the zwitterionic groups provides fouling resistance (Yang et al., 2014c). Tripathi et al. proposed a distinctive and modest method for the assembly and selective surface modification of a pH-responsive nanoporous membrane with antifouling and antibiofouling properties. The membranes were fabricated by selective surface modification of polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) diblock copolymers by quaternization (PS-P4VP-Q) and zwitterionization (PS-P4VP-Z) reactions on P4VP moiety. Antifouling and antibacterial properties were examined by studying the adsorption of bovine serum albumin protein and bacterial cell attachment. At pH 4, PS-P4VP exhibited a positively charged nature due to protonation of the pyridine moiety, which deterred the positively charged BSA [fluorescein isothiocyanate (FITC)-conjugated albumin bovine] protein due to electrostatic repulsion. However, the net protein adsorption on both PS-P4VP

and PSP4VP-Q was higher than that on PS-P4VP-Z under both pH 4 and 7. PS-P4VP-Z showed minimum BSA adsorption among all the prepared films due to strong hydration of the surface. The modified membranes bear permanent positively charged groups and that played an important role. The adhesion and growth of biofilms of both *Escherichia coli* and *Staphylococcus epidermidis* were found to be higher on the PS-P4VP than on the PS-P4VP-Q or PS-P4VP-Z films. The fluorescence images supported the good antibacterial activity of the modified films (Tripathi et al., 2013).

Amphiphilic polymer films have been projected as a prospective approach to combat marine biofouling (Callow & Callow, 2012). The surface structures with mixed hydrophilic and hydrophobic functionalities and nanoscale heterogeneities can prevent/diminish settlement of organisms and biomolecule-substrate interactions (Hawkins et al., 2014; Martinelli et al., 2015; Bauer et al., 2016; Faÿ et al., 2016; Martinelli et al., 2016). Oliva et al. synthesized surface-active amphiphilic diblock copolymers (Si-EFS14 and Si-EFS71) consisting of poly(dimethylsiloxane) (PDMS) and poly(4-(triethyleneglycol monomethyl ether)-2,3,5,6-tetrafluorostyrene) blocks by ATRP. Films were prepared by integrating 4 wt.% of each copolymer into the PDMS matrix (to enable the dispersion of the copolymer), along with a block of para-functionalized fluorostyrene (with a triethylene glycol chain) to modify the surface chemistry. Bioassays were implemented on the films using

two barnacle species (*Balanus amphitrite* and *Balanus improvisus*). The results showed that the antifouling capability is not greatly affected by the chemistry of the amphiphilic additive, whereas the fouling release properties depend on its hydrophilic/hydrophobic balance. Both the barnacle species at the larval stage appeared to favor settling on films containing Si-EFS14 rather than on those comprising Si-EFS71 (the outer layer of latter film had a greater content of hydrophilic oxyethylene units than the former). The juveniles of *B. improvisus* were more easily released from films containing Si-EFS14 compared to those with Si-EFS71, which suggested that removal was favored when a lower amount of oxyethylene units was located at the surface (Oliva et al., 2017).

Polymer networks with supramolecular blocks demonstrated several properties that are beneficial for slippery, self-lubricating polymers. The lubricating layer is expected to be an extremely smooth, constantly lubricated liquid interface, which can reduce contact angle hysteresis and adhesion of external matter. The polymer can be modified to include both covalent and supramolecular cross-linking. Upon swelling, in addition to favorable interaction with the polymer segments, a suitable amount of good solvent will disrupt the physical cross-linking, allowing the polymer to swell to an even greater extent. The degree of swelling and/or the rate of swelling can be increased or decreased by adjusting the size of the polymer component, the nature of the supramolecular moieties, and the relative proportions of the two. The swellable polymer composition includes a main polymeric network with supramolecular inclusions, generally having the formula P_xS_y , where P is a covalently cross-linked polymer and S is a supramolecular block within this polymer network ($x+y=1$, and y can be from 0 to 1; 0 corresponds to a simple polymer with no supramolecular addition). In the P block, the repeat units and length of the polymer chains can be changed to mediate the degree of cross-linking (and thus the degree of swelling) and mechanical properties. Variation in the S blocks can be used to control the strength of the cross-linking and the rate of the polymer network formation. The cross-linker is dynamic and upon polymer cracking (e.g. damage) can diffuse through the polymer to the crack position and fully recover it (Aizenberg et al., 2015).

Cui et al. reported a secretion system that consisted of liquid storage compartments (droplets) in a supramolecular polymer-gel matrix and demonstrated that a dynamic liquid exchange between the compartments, matrix, and surface layer allowed recurrent, responsive surface lubrication and matrix healing. Diminution of the surface liquid or local material damage prompted secretion of the

stored liquid via a dynamic feedback between polymer cross-linking, droplet contraction, and liquid transference, which can be read out through the changes in the system's optical transparency. This process creates and restores an extremely slippery, fouling-resistant surface. The primary requirement for fabricating such a system was a polymer with chemical affinity to the stored liquid and with bonding strength strong enough to stabilize the droplets and weak enough to allow bond reconfiguration and hence inducible secretion, which was met by the supramolecular polymer. The supramolecular design involved copolymers of urea and PDMS, which reversibly cross-linked via H bonding of the urea units, where differences in the spacer units caused different cross-linking strengths. When the polymer was dissolved in a volatile solvent along with an excess of secretion liquid, rapid solvent evaporation can occur, which can trigger polymer cross-linking, trapping some of the secretion liquid within the network while leaving the excess to form droplets (Cui et al., 2015).

Hydrogels derived from natural, synthetic polymers or non-polymeric compounds have materialized as a prospective platform for biofouling applications. Entrapped molecules in the hydrogel matrix could be manipulated with on-demand release properties initiated by external/internal stimuli (Kim et al., 2017). Several attempts were devoted to develop antifouling/antimicrobial hydrogels based on PEGylated polymers (Liu et al., 2012), zwitterionic polymers (Mi & Jiang, 2012), acrylate-based systems (Li et al., 2011), polyelectrolyte complexes (Tsao et al., 2010), and self-assembled peptides (Salick et al., 2007). Inorganic-organic hybrid nanocomposite hydrogels, POSS-based dendrimers (Cordes et al., 2010), etc., are also investigated in this line.

Lian et al. reported an innovative bio-inspired supramolecular inorganic-organic hydrogel with excellent anti-biofouling capability and tunable mechanical strength via ionic interaction between sodium polyacrylate (negatively charged) enfolded clay nanosheets and POSS core-based generation 1 (L-arginine) dendrimer (POSS-R) (positively charged). With the increase in POSS-R concentration, the hydrogels become more compact, complemented by noteworthy higher mechanical strength. Importantly, they showed excellent antibiofouling properties, as was evident from the results of the cell attachment studies (MC3T3 cells) by fluorescence imaging. The non-covalent cross-linking approach for the development of the supramolecular hydrogels gifted them with prompt thixotropic response and shape memory functions (Lian et al., 2018).

Li et al. reported an effective approach to generate stimulus-responsive antimicrobial gel formed from

stereocomplexation of biodegradable poly(l-lactide)-*b*-poly(ethylene glycol)-*b*-poly(l-lactide) (PLLA-PEG-PLLA) and a charged biodegradable polycarbonate triblock polymer (i.e. PDLACPC-PDLA). The PLLA-PEG-PLLA triblock copolymers produced have very narrow molecular weight distributions. Analogous triblock polymers were then replicated using d-lactide (i.e. PDLA-PEG-PDLA) for the corresponding stereocomplexation studies. It was found that PEG polymers of more than 6 kDa allowed complete polymer dissolution in aqueous media assuming lactide blocks remained at or under 1 kDa. A cloud point temperature and gelation upon heating the polymer solution above 60°C were observed. The solutions on incubation (at 37°C for 5 h) formed opaque, low modulus, and viscous solutions at polymer concentrations of 13.2% (w/v). Optical microscopy images of PLLA-PEG-PLLA showed an abundance of fiber-like nanostructures, whereas PDLA-PEG-PDLA formed far less fiber-like assemblies. Studies against clinically isolated microbes indicated that the gels were effective in inhibiting the growth completely and showed an almost impeccable killing efficiency (~80% of bacterial cells killed) (Li et al., 2013).

Chapman et al. patented a gel coating that was composed of one or more organogelators whose molecules can establish intermolecular physical interactions leading to self-assembly with 3D network/nanoweb gel formation. The H-bonded organogelators were characterized by at least two N-H bonds per molecule, wherein the N atoms are bound to at least one carbonyl group, and the preferred ones were from the group of urea, ureido-pyrimidone, ureido-triazine, amide, urethane, or their mixtures. The mixture comprising a solvent and organogelators was applied on a porous support and subsequently processed to form a nanoweb gel, then the solvent was removed, leaving a porous nanoweb coating (Chapman et al., 2007).

Superhydrophobic polymeric surfaces can be made by lowering the surface energy and by the addition of suitable surface structures (Chen et al., 2014; Xue et al., 2014a). Wei et al. reported a low-molecular-weight gelator as a means to prompt fabrication of superhydrophobic as well as liquid-infused slippery surfaces. This was achieved by drop-casting solutions of (±)-N,N'-(trans-cyclohexane-1,2-diyl) bis (2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-amide) onto glass followed by solvent evaporation resulting in a 3D fibrous superhydrophobic surface, which was used as a matrix to immobilize a perfluorinated lubricant effectively. The slippery surface displayed quick self-healing under ambient conditions (when mechanically scratched) with an enhanced liquid repellency against water/low-surface-tension liquids. The H bonding-mediated polymerization and the perfluorination of the side

chains played a synergistic role in achieving superhydrophobicity. The study showed that such a gelator fibrous network could be efficiently utilized to capture lubricants and can greatly help in improving liquid repellency (Wei et al., 2014b).

4.2 Nanocontainer-based host-guest systems

Similar to systems reported in § 2.2, several works on smart on-demand biocide-release coatings employing supramolecular host-guest interactions are reported. A recent review by Yang et al. is available where the authors provided an account on stimuli-responsive host-guest supramolecular assemblies for engineering multifunctional biosurfaces that includes photo-controlled, redox chemistry-controlled, guest competition-controlled, pH-controlled, and orthogonal stimuli-responsive biointerfaces (Yang et al., 2014b). The following section highlights recently reported interesting works on CDs and mesoporous silica-based host-guest systems.

4.2.1 Mesoporous silica-based

Research has proved that self-assembly on the exterior surface of MSNs is an effective approach for the fabrication of antibacterial nanomaterials (Ambrogio et al., 2011; Li et al., 2012; Tarn et al., 2013; Tao et al., 2015). Pezzoni et al. have shown that supramolecularly templated mesoporous silica coatings achieved by an evaporation-induced self-assembly with regulated pore size considerably reduced bacteria attachment. The authors performed two types of assays [submerged and air-liquid interface (ALI)]. The surfaces remained completely covered by the cell suspension in the former method, whereas around half of the surfaces were covered in the latter. The assays were conducted with *Pseudomonas aeruginosa*, and the results (Figure 12) showed the effect of the nanoporous silica coatings on the number of viable cells [colony forming units (CFU)] in 4-, 8-, and 24-h-old biofilms. Even though no marked difference was observed after 4 h of incubation, with longer time of incubation, the number of adhered cells to MS-4 and MS-9 (mesoporous surfaces with average pore diameters of 4 and 9 nm, respectively) in the submerged systems significantly lowered when compared to the smooth surfaces, and the variation was higher in the ALI systems. The whole biofilm mass in the control [non-nanoporous silica (NMS); Figure 12] and test surfaces was assessed by staining with crystal violet. Stained 24-h

Figure 12: (A) Effect of mesoporous surfaces (MS) on the average numbers of attached cells (quantified by the plate count method). Submerged and ALI biofilms were grown on mesoporous MS-4 and MS-9 surfaces (NMS, control surface). (B) Effect of mesoporous surfaces on the formation of biofilm assessed by crystal violet staining (by measuring absorbance at 575 nm) (reproduced with permission from Pezzoni et al., 2017; Copyright @ Elsevier).

biofilms clearly demonstrated the inhibitory effect of the coatings on biofilm formation (Figure 12). A significant reduction in absorbance (at 575 nm) was observed with the mesoporous surfaces when compared to the control (Figure 12) (Pezzoni et al., 2017).

To avoid the adverse cytotoxicity of the cationic polymers, a few works investigated the supramolecular assemblies of bis-aminated polymer with cucurbit[7]uril (CB[7]) (Liu & Du, 2010; Shetty et al., 2015). In a recent work, Li et al. reported a new nano-assembly made from amoxicillin (AMO), MSN, 1,2-ethanediamine (EDA)-modified polyglycerol methacrylate (PGEDA), CB[7], and TPE-based tetracarboxylic acid, namely, TPE-(COOH)₄ (Figure 13). AMO was loaded into the mesopores of MSNs and then CB[7] was used to interact with PGEDA to form stable supramolecular polymers on the MSN surface via ion-dipole interactions. Negatively charged TPE-(COOH)₄ could further bind with positively charged supramolecular polymers on the MSN surface via electrostatic interactions to form an LbL supramolecular nano-assembly. When bacteria contacts with this nano-assembly, the binding of the anionic bacterial surface toward the cationic PGEDA layer can decrease/disrupt the interactions between the PGEDA and TPE-(COOH)₄ layers, leading to reduced TPE-(COOH)₄ emission. Besides, upon the addition of adamantaneamine

(AD), a more stable AD ⊂ CB[7] complex was formed and PGEDA is liberated through competitive replacement; this directed to the release of AMO, resulting in a higher antibacterial property. Studies on the antibacterial activities of nano-assembly toward *Escherichia coli* and *Staphylococcus aureus* showed that MSN-PGEDA-CB[7]-TPE with AD displayed high killing efficiency (99%) toward *E. coli*, while killing efficiency was >30% in the absence of AD (Figure 13). The results provided further evidence to the fact that the antibacterial ability of a nano-assembly can be regulated by an appropriate supramolecular disassembly process (Li et al., 2017).

Zheng et al. reported a pH/sulfide ion-responsive multi-functional release system based on MSNs loaded with a corrosion inhibitor (BTA) and antibacterial agent (benzalkonium chloride or triclosan). To realize this, the outer surface/mesoporous orifice of MSNs was initially functionalized with N-(3-trimethoxysilylpropyl) ethylenediamine (DiA) to form DiA-MSNs. Subsequently, the functionalized MSNs were loaded by BTA and biocides with a different molar ratio through a vacuum method. The loaded nanocontainers were recovered by centrifugation and washed to remove excess absorbed BTA and biocides. Lastly, an aqueous CuSO₄ solution was dropped on the powder of the loaded nanocontainers to form an

Figure 13: (Left) Schematic illustration of the nano-assembly and likely mechanism for bacterial detection and inhibition. (Right) Colony forming units for *Staphylococcus aureus* and *Escherichia coli* treated with nano-assembly before and after the addition of AD on LB agar plate (reproduced with permission from Li et al., 2017; Copyright @ The American Chemical Society).

insoluble complex with BTA at the mesopore orifices, obtaining $\text{Cu}_x\text{-(y)@DiA-MSNs}$, where x is the concentration of the CuSO_4 solution and y is the molar ratio of the biocide to BTA in the first loading cycle. The inhibitor/antibacterial agent's release was triggered when the pH is <5 or the $[\text{S}^{2-}]$ is $>0.02 \text{ mM}$ ($\sim 0.6 \text{ ppm}$) (Zheng et al., 2013).

4.2.2 CD based

CDs are widely used as a guest in host-guest complex formulations in the construction of nanosized objects for biocide encapsulation. Véronique and Loïc have reviewed CDs in biocidal applications highlighting several examples of biocide-CD inclusion complexes. The biocide-CD complexation improves (i) the physicochemical properties of the biocides (improved aqueous solubility, decreased vapor pressure, etc.), (ii) the controlled release and bio-availability, (iii) the shelf-life, (iv) the storage conditions, and (v) the environmental friendliness (Véronique & Loïc, 2014; Zhao et al., 2018a).

CDs have been shown to be effective for the inactivation of pathogens; however, a high CD concentration ($>5 \text{ mM}$) needs to be maintained for efficient biocidal activity. Leclercq et al. have shown that CDs can remarkably boost the virucidal activity of di-n-decyl dimethyl

ammonium chloride, where they work synergistically with the biocide providing an apparent decrease in the active virucide concentration between 40 and 85% (Leclercq et al., 2012). Their mechanism of action is based on the lipid extraction from the cell membrane driven by complexation (Leclercq et al., 2016).

Wen et al. showed that the electrospun polylactic acid (PLA)/cinnamon essential oil (CEO)/ β -CD nanofilm had outstanding antimicrobial activity against both gram-positive and gram-negative bacteria. They have fabricated a novel antimicrobial packaging material by integrating the CEO/ β -CD inclusion complex (CEO/ β -CD-IC) into PLA nanofibers. The CEO/ β -CD-IC was fabricated by the coprecipitation method. SEM and FTIR spectroscopy studies confirmed complex formation with enhanced thermal stability. The complex was subsequently assimilated into PLA nanofibers (by electrospinning) and studied for their antimicrobial activity. The minimum inhibitory concentration of the nanofilm against *Escherichia coli* and *Staphylococcus aureus* was approximately 1 mg ml^{-1} when compared to the equivalent CEO concentration of $11.35 \text{ } \mu\text{g ml}^{-1}$. The corresponding minimum bactericidal concentrations were approximately 7 and 79.45 mg ml^{-1} , respectively (Wen et al., 2016).

Cai et al. developed a host-guest chemistry-based biomimetic approach for the fabrication of antifouling

titanium (Ti) oxide surfaces. Two catecholic derivatives, dopamine 4-(phenylazo) benzamide (AZODopa) and dopamine 1-adamantanecarboxamide (AdaDopa), were respectively produced via simple reactive ester-amine reaction and amidation, and immobilized onto the Ti oxide surfaces to form guest molecule monolayers for the successive host-guest interactions with zwitterionic heptakis[6-deoxy-6-(N-3-sulfopropyl-N,N-dimethylammonium ethyl sulfanyl)]- β -CD (SBCD) and hydrophilic β -CD polymer (CDP) (Figure 14). The elemental composition and hydrophobic/hydrophilic properties of the oxide before and after modification were characterized by XPS and static water contact angle measurements, respectively, and the results showed that the oxide surface had been successfully functionalized. The protein adsorption studies (quantified by XPS N 1s and C 1s peak area ([N]/[C]) ratio) showed a significant increase in [N]/[C] ratios for the pristine Ti oxide, Ti oxide-Ada, and Ti oxide-AZO surfaces, indicating that these surfaces can adsorb bovine plasma fibrinogen (FBG)

easily (Figure 14). In comparison to the corresponding Ti oxide-Ada and Ti oxide-AZO surfaces, the increase in [N]/[C] ratios was marginal for the Ti oxide-Ada@SBCD (from 0.06 to 0.08) and Ti oxide-AZO@SBCD (from 0.07 to 0.09) surfaces after the FBG exposure. The minor change in [N]/[C] ratio before and after FBG exposure for the oxide surfaces functionalized with zwitterionic SBCD suggested that the non-specific adsorption of FBG can be greatly inhibited. The results on *Escherichia coli* adhesion, via the spread plate method (Figure 14), showed that there is an apparent decrease in the number of attached bacterial cells on the Ti oxide-Ada@SBCD, Ti oxide-AZO@SBCD, Ti oxide-Ada@CDP, and Ti oxide-AZO@CDP surfaces when compared to the pristine and the AdaDopa- and AZODopa-anchored Ti oxide surfaces (Cai et al., 2016).

Magnetic iron oxide nanoparticles (MNPs) have high physical/chemical stability and good biocompatibility, and they offer a high surface area for post-modification. A few works reported on β -CD-modified MNPs for

Figure 14: (A) Schematic design of a biomimetic technique to fabricate guest molecule-anchored Ti oxide surfaces and a supramolecular assembly to fabricate SBCD- and CDP-functionalized Ti oxide surfaces via host-guest complexation. (B) Evaluation of protein adsorption, expressed as XPS-derived [N]/[C] ratios on different surfaces after incubation in PBS (pH 7.4) containing 1 mg ml⁻¹ of FBG for 12 h. (C) Number of adhered bacterial cells per cm² on different surfaces after exposure to *Escherichia coli* suspension in PBS (1 × 10⁷ cells ml⁻¹) for 4 h (reproduced with permission from Cai et al., 2016; Copyright @ Elsevier).

incorporation of adamantane (Ada) derivatives to immobilize proteins and other biomolecules (Díez et al., 2012; Lai et al., 2017). The β -CD-Ada pair is attractive owing to the specific and comparatively robust binding interactions, and they have been employed as the building block for creating complex structures. In this direction, Hu et al. reported a supramolecular host-guest system for biofunctionalization of MNPs. The production scheme (Figure 15) shows that, firstly, the porous Fe_3O_4 particles stabilized by citrate groups were produced via a one-pot hydrothermal method. A thin layer of dense silica was successively coated on the MNP surface by using the sol-gel method to yield a core-shell structured MNP@SiO_2 . Ada-terminated organic silanes were subsequently introduced on the surface of the MNP@SiO_2 particles via the silane coupling technique to obtain MNP@SiO_2 -Ada composite particles. To explore the versatility, these particles were further incorporated with CD-X molecules (biofunctional β -CD derivatives, where X is the bioactive

ligand conjugated on the narrower rim of β -CD). Three different CD-X molecules with X=biotin (B), mannose (M), or quaternary ammonium salt (QAS) were used. To test whether the functionalized particles displayed the agreeing activity, pristine MNPs and MNP@SiO_2 -M particles (1 mg ml^{-1}) were incubated in a FITC-concanavalin A (ConA) solution for 20 min, and the binding abilities were compared. Similar to the MNP@SiO_2 -B particles, the MNP@SiO_2 -M particles showed a high binding capacity to the target protein ConA, at a rate ~ 8.3 times greater than that of pristine MNPs. Furthermore, these particles also presented resistance to adsorption of the non-specific protein BSA. To test the bactericidal properties, pristine MNPs and MNP@SiO_2 -Q particles [2 mg ml^{-1} in phosphate-buffered saline (PBS)] were incubated in a model pathogenic bacterium *Staphylococcus aureus* suspension (10^5 CFU ml^{-1} in PBS, 3 h), and the bacterial viability was quantified using a conventional colony-counting assay. From Figure 15, it is clear that MNPs themselves could

Figure 15: (A) Preparation method for MNP@SiO_2 -Ada and integration with CD-X. (B) Adsorption of 0.1 mg ml^{-1} FITC-ConA on MNP and MNP@SiO_2 -M. (C) The bacterial capture efficiency of MNP and MNP@SiO_2 -M for *Escherichia coli*. Error bars denote the standard deviation of the mean ($n = 3$). (D) Typical photos of *Staphylococcus aureus* colonies formed on agar plates at a density of $1 \times 10^5 \text{ CFU ml}^{-1}$ (a) and after being treated with MNP (b) and MNP@SiO_2 -Q (c) for 3 h (reproduced with permission from Hu et al., 2018; Copyright @ The Royal Society of Chemistry).

not kill bacteria, whereas the CD-Q-functionalized MNPs showed good biocidal activity that killed >99% bacteria, which was attributed to the copious QAS groups that can disrupt the negatively charged cell membranes (Hu et al., 2018).

4.3 Metal-organic structures

Suitably modified MOFs have been projected as apt materials for superhydrophobic applications (Nguyen & Cohen, 2010; Bétard et al., 2012; Rao et al., 2014). Roy et al. reported a self-cleaning MOF having high water contact angles. Coordination-driven self-assembly of dialkoxyoctadecyl-oligo-(p-phenyleneethynylene) dicarboxylate (OPE-C18) with Zn(II) in a DMF/H₂O mixture led to a 3D supramolecular porous framework {Zn(OPE-C18)·2H₂O} (NMOF-1) with high thermal and chemical stability. The superhydrophobicity in NMOF-1 (water contact angle, 160–162°) was attributed to the reduced surface free energy due to the periodic organization of 1D Zn-OPE-C18 chains with octadecyl alkyl chains projecting outward (Roy et al., 2016). Ogawa et al. reported electrospun fluoroalkyl silane (FAS)-modified LbL structured film. The rough fiber surface produced by the electrostatic LbL coating of TiO₂ nanoparticles and poly(acrylic acid) (PAA) was utilized. The results disclosed that the FAS modification was the main process in augmenting the surface hydrophobicity. A TiO₂/PAA film-coated cellulose acetate nanofibrous membrane with FAS surface modification displayed a maximum water contact angle of 162° and a lowest water-roll angle of 2° (Ogawa et al., 2007). These novel water-repellent materials are suitable for self-cleaning antibiofouling applications (Bixler & Bhushan, 2012; Liu et al., 2017).

The supramolecular metal-phenolic networks such as the tannic acid (TA)-Fe(III) coordination complexes offer a modest and green route for modifying antifouling membranes (Ju et al., 2015). Park et al. demonstrated a rapid spray-assisted nanocoating of supramolecular metal-organic coordination complexes (MOCs) of TA and ferric ions [Fe(III)-TA-MOC], where the concurrent spraying of Fe(III) and TA led to a uniform film. The coating was studied with various substrates, including Au, Si/SiO₂, Ti, Al, Ag, Cu, Ni, Sn and Zn foil, SS, PS, and polytetrafluoroethylene. All the substrates studied turned out to be hydrophilic (contact angle ~35°) irrespective of their hydrophobicity before the coating. The study also showed that the coating effectively barred the growth and proliferation of *Trichophyton rubrum* (Park et al., 2017).

Yin et al. reported an antifouling liquid-infused enamel surface for dental biomaterials where a micro/nanoporous surface achieved by H₃PO₄ etching was subsequently functionalized by hydrophobic heptadecafluoro-1,1,2,2-tetrahydro decyl trichlorosilane. Successive infusion of fluorocarbon lubricant (Fluorinert FC-70) into the polyfluoroalkyl-silanized rough surface created a slippery liquid-infused porous surface (SLIPS). The antibiofouling properties evaluated by salivary proteins (mucin, *Streptococcus mutans*) adsorption *in vitro* and dental biofilm formation (rabbit model) *in vivo* demonstrated that the surface SLIPS considerably prevented mucin adhesion, *S. mutans* biofilm formation, and plaque formation (Yin et al., 2016).

Several works are reported on the organotin (IV)-based complexes; however, they are unattractive due to environmental regulations (Omae, 2003; Chauhan & Shaik, 2005; Rehman et al., 2009; Shujah et al., 2011).

Enzyme mimics or artificial enzymes have shown immense potential in the development of antibiofouling systems (Gale & Steed, 2012; Natalio et al., 2012). Examples include CD-based (Marchetti & Levine, 2011), calixarenes-based (Tabakci et al., 2012; Rebilly et al., 2015), zeolites-based (Weckhuysen et al., 1996), and MOF-based (Larsen et al., 2011) systems. More details on enzyme mimics are described elsewhere (Xue et al., 2014b; Kuah et al., 2016; Gu et al., 2017). A number of reports on biological supramolecules are available, which is out of the scope of this review.

5 Future potentials

During the past four decades, supramolecular chemistry has grown into a foremost field of interest to scientists across different disciplines including corrosion science and technology. The ongoing research efforts in understanding the fundamental nature of non-covalent interactions and design/synthesis of novel supramolecules are expected to benefit hugely in the development of highly corrosion resistant, prolonged self-healing, and superior antibiofouling surfaces.

An area that is expected to provide significant technological advancements is the smart on-demand release coatings with encapsulated inhibitors/biocides. Despite a significant number of research efforts in this direction, there are only a few commercially available products (Stankiewicz & Barker, 2016). The design and preparation of novel host-guest chemistry-based nanocontainers with multipurpose functionalities are expected to deliver

great prospects for developing new-generation coatings. More research works need to be performed in achieving sustained-release capsules for a longer period of service. Further works are desirable to optimize the nature and extent of important additives in a selected smart coating so that optimum conditions can be derived where the additives do not deteriorate but enhance the mechanical strength, coating adhesion, and barrier properties. It has been suggested that future research should also focus on the progress and application of siloxane technology, as well as the development of smart self-healing metallic coatings with improved hardness and wear resistance (Stankiewicz & Barker, 2016). Hydrogels can further be explored as stimuli-responsive nanocapsules, especially for biofouling applications. Some reported works available in the recent literature (Nowacka et al., 2015; Narinder et al., 2017) have the potential for applicability in corrosion and biofouling research.

Significant advancements have been achieved in the concept of supramolecular polymerization: the self-assembly of monomers into polymeric structures through the exploitation of non-covalent interactions. Challenges remain in achieving stable and clear-cut macroscopic supramolecular assemblies for different functions including corrosion and biofouling. By increasing the density of the building blocks, the driving force for the assembly can be transformed suitably to develop hydrophobic or hydrophilic surfaces. The “flexible spacing coating” (Cheng et al., 2014) concept can be explored further. More studies on metal-ligand macroscopic self-assemblies (Akram et al., 2017) are demanding.

Studies on functionalized supramolecular PUs with partial replacement of covalent bonding can yield optimum self-healing coating compositions without losing mechanical and barrier properties. More studies on natural polymers such as CDs in designing sustained-release smart coatings with commercialization prospects are required. Novel biopolymers such as eumelanin (dihydroxyindole oligomers) can be investigated. Calixarenes need to be further explored in the construction of enzyme mimics and host-guest chemistry-based coatings and inhibitors. Advanced works on hairy inorganic nanoparticles (assembling polymer-coated nanoparticles into hybrid nanocomposites with targeted architectures) (Yi et al., 2017) for the development of functional multi-hierarchical nanocomposites can yield fruitful results.

More works on chitosan-based supramolecular compounds in biofouling applications can yield better results, as it has good antimicrobial, antifungal, and antialgal properties. CDs can be immobilized at the 6-OH position of chitosan to retain the functions of the 2-NH₂ group (Chen

et al., 2016). Studies have shown the antifouling potential of the chitosan-based systems such as chitosan-ZnO nanocomposite hybrid coatings (Al-Naamani et al., 2017). Another natural material, lignin, can be studied further in this direction and is suitable as a matrix in LbL films. Lignin-based supramolecular antibiofouling coatings can be used as an overcoat on the conventional barrier coat. Cerrutti et al. have shown that incorporation of lignin can enhance the mechanical properties and thermal stability of coatings and can act as effective diffusion barriers in anticorrosion coatings for steel in the saline environment (Cerrutti et al., 2015).

Modifying the supramolecular interactions in developing superhydrophobic surface is a critical area. More research on gel systems in developing superhydrophobic and liquid-infused slippery surfaces will be beneficial. The gel-based coatings are attractive and can be used as a top layer coating over the corrosion protective barrier coating and can function as on-demand release smart systems for inhibitors, biocides, and lubricants, which is particularly relevant in biofouling applications. The concept of the flexible spacing coating can further be explored to modify the polymer gel systems so that reversible macroscopic assembly with rigid building blocks can be realized (Cheng et al., 2014).

Among the different non-covalent interactions, metal-ligand interactions are particularly interesting and may lead to more robust supramolecular assemblies. Metal-ligand polymers can be further explored for corrosion and biofouling protection. The advantage of the tunable property of these compounds can be utilized. A few recently reported works have the potential to be applied in the area of corrosion and biofouling prevention (Ozaki et al., 2017; Leoni & Cort, 2018; Piot et al., 2018; Shao et al., 2018). Studies on novel supramolecular MOF-based composites having supreme mechanical, barrier, and superhydrophobic properties can yield commercially relevant materials. Metal ion-induced self-assembly of metallosupramolecular coordination polyelectrolytes can further be explored. Studies on self-cleaning MOFs (with inherent thermal and chemical stability) having high water contact angles and corrosion resistance can yield desirable results for producing bio-inspired self-cleaning surfaces for advanced antibiofouling paints (Roy et al., 2016). The MOFs with inherent corrosion inhibition characteristics can further be loaded with effective corrosion inhibitors, and the adsorbed molecules can function as a sustained-release system at the metal/electrolyte interface.

For fabricating materials with high mechanical performance and self-healing/antibiofouling ability,

nacre-inspired composites (Zhao et al., 2018b) with supramolecular modified surfaces can be investigated. Studies in this direction can lead to mechanically robust materials with self-healing properties (Hart et al., 2014). More works on dendrimers, graphene, and fullerene derivatives can be utilized in fabricating supramolecular assemblies for corrosion and biofouling prevention. Efforts need to be put forward in improving the stability and selectivity of host-guest complexes, e.g. crown ether-based host-guest complexes. More studies on crown ether dendrimer complexes (Winkler et al., 2009) can yield desirable results.

6 Summary and outlook

This work provides a comprehensive review of the application of supramolecular chemistry in corrosion and biofouling prevention. The research advancements in this area were explained under three subheads: surface coatings, corrosion inhibitors, and antibiofouling surfaces. In each section, advancements in polymeric, host-guest-based systems, organic-inorganic hybrid systems, and other supramolecular structures and techniques were incorporated.

The primary area of research interest in surface coatings where supramolecular interactions come into play is indeed the on-demand release smart coatings. The current trend shows that most of the reported works in this area are focused on CDs and mesoporous silica-based host-guest systems. The most widely investigated synthetic polymer in this direction is the PU. Studies indicated that an optimum ratio needs to be achieved between the covalent and the non-covalent networks of PUs to provide a suitable self-healing effect without losing barrier properties.

The third-generation supramolecules such as CDs, calixarene, and crown ethers were investigated as effective corrosion inhibitors, especially as slow-release embedded inhibitors. Among them, CD-based systems have a high potential to realize slow- and controlled-release host-guest systems. Many studies are reported on coordination polymers and MOFs in corrosion inhibition applications. A few works are available on functionalized PU inhibitors.

Polymeric materials are widely employed in antibiofouling applications. Polymer gel-based systems are projected as future candidates, especially as a commercially relevant topcoat over the corrosion protection barrier coating. Several studies have investigated host-guest-based biocide-release coatings. MOFs can be

attractive in developing superhydrophobic antibiofouling surfaces.

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Bionote

Viswanathan S. Saji

Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia, saji.viswanathan@kfupm.edu.sa

Viswanathan S. Saji is a Research Scientist III at the Center of Research Excellence in Corrosion, King Fahd University of Petroleum and Minerals, Saudi Arabia. He received his PhD (2003) degree from the University of Kerala. He was a Research Associate at IIT Bombay (2004–2005) and IISc Bangalore (2005–2007), Postdoctoral Researcher at Yonsei University (2007–2008) and Sunchon National University (2009), Senior Research Scientist at UNIST (2009–2010), Research Professor at Chosun University (2008–2009) and Korea University (2010–2013), and Endeavour Research Fellow at the University of Adelaide (2014).