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Ionic self-assembly of redox-active polyelectrolyte-surfactant complexes: mesostructured soft materials for electrochemical nanoarchitectonics

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Abstract

Ionic self-assembly (ISA) has emerged as a powerful nanoarchitectonics strategy for constructing functional supramolecular materials through electrostatic interactions. This approach enables the formation of highly ordered nano- and mesostructures with tunable electrochemical properties. A key application of ISA lies in electroactive polyelectrolyte-surfactant complexes, which serve as dynamic platforms for biosensing and electrochemical devices. These materials, easily integrated onto electrodes via solution-based deposition techniques, offer tailored charge transport and redox activity. Their ability to incorporate metal nanoparticles and enzymes further expands their functionality, enabling the development of amperometric biosensors for highly sensitive biochemical detection. This review explores the principles of ISA-derived materials, emphasizing their role in electrochemical applications and their potential in next-generation biosensors.

Keywords: nanoarchitectonics, bioelectrochemistry, self-assembly, polyelectrolyte-surfactant complexes, electroactive materials

1. Ionic Self-Assembly

Among the various self-assembly techniques, ionic self-assembly (ISA) has emerged as a particularly effective method for creating nanostructured materials.[1] ISA capitalizes on the strong electrostatic interactions between oppositely charged species to drive the formation of well-organized assemblies.[2] This approach has garnered significant attention in recent decades due to its versatility, efficiency, and ability to produce materials with highly tunable properties.[3,4] The capability of ISA to control material morphology, porosity, and functionality has led to its application across a wide range of fields, including biomedicine, electronics, environmental science, and catalysis.[5-7]

The exploration of materials based on the interactions between surfactants and polyelectrolytes began as early as the 1970s. Researchers such as Gooddard and Hannan at Union Carbide Corporation investigated the interactions between sodium dodecyl sulfate and water-soluble cationic cellulose ether (known as Polymer JR).[8-10] Around the same time, Buckingham and his colleagues at Unilever (UK) studied the interactions of polylysine with SDS.[11,12] It is notable that both research groups were associated with industry rather than academia, as the combination of polyelectrolytes and surfactants offered immediate practical applications. By the 1980s, surfactant-polyelectrolyte systems were extensively studied from a physicochemical perspective.[13,14] The 1990s saw a systematic approach to developing supramolecular materials based on polyelectrolyte-surfactant complexes, highlighted by the influential paper by Antonietti and co-workers[15] in which polyelectrolyte-surfactant complexes were introduced as a new type of solid, mesomorphous material.[16,17] Since then, the concept has been embraced by the chemistry and materials science communities, combining with other approaches to create a diverse array of organized molecular systems for various applications.[18,19]

From a broader perspective, the potential of surfactants to interact electrostatically with polyelectrolytes and simultaneously provide organization and structure was relatively underexplored until then. With the rise of systematic studies on ISA-based materials in the 1990s, researchers began to realize that electrostatic forces - stronger and more directional than other noncovalent interactions - could be harnessed to drive the self-assembly of charged molecules into highly ordered structures.[20,21] This insight led to the development of ISA as a distinct and powerful method for material design, offering unique advantages over other self-assembly techniques.

ISA represents a significant advancement in self-assembly, providing a novel paradigm for constructing materials that mimic the hierarchical organization found in biological systems. By using electrostatic interactions as the primary driving force, ISA enables the creation of complex structures with properties that can be precisely tuned through careful selection of building blocks and assembly conditions. This versatility has made ISA a highly attractive method for a broad range of applications, from the development of nanostructured membranes and coatings to advanced drug delivery systems and electronic devices.[22-28]

At its core, ionic self-assembly (ISA) relies on electrostatic interactions, which arise from the attraction between oppositely charged species. These interactions drive the self-assembly process by bringing together charged surfactants and building blocks to form organized structures.[29] The strength and directionality of electrostatic interactions make them particularly effective for controlling the properties of the final material. In ISA, building blocks typically include charged surfactants and oppositely charged polyelectrolytes.[30] Surfactants, due to their amphiphilic nature, are especially well-suited for ISA, as they can act as structure-directing agents facilitating self-organization.[3132]

A distinctive feature of ISA is its cooperative binding mechanism, where initial electrostatic interactions between charged species promote further binding, leading to the progressive formation of the final structure. This cooperative process not only increases the reliability of ISA but also enables the creation of complex, hierarchical materials with properties tailored to specific applications. The thermodynamics of ISA is governed by the balance between enthalpic and entropic contributions.[33] The electrostatic attraction between oppositely charged species provides a favorable enthalpic contribution, while the organization of surfactants and building blocks improve the hydrophobic interactions, and the liberation of small molecules, increasing the entropy, all in all the process becomes spontaneous. Nonetheless, the process is also sensitive to ionic strength, pH, and solvent, which may influence the completion of the self-assembly process.[34]

Kinetics also plays a crucial role in ISA, influencing both the rate of the assembly process and the stability of the final structure. The assembly process is often kinetically controlled, meaning that factors such as temperature, pH, and ionic strength can be adjusted to modulate the rate of self-assembly.[35] These parameters can be fine-tuned to achieve desired material properties, such as size, shape, and porosity. ISA is characterized by its high degree of tunability, allowing for the creation of a wide range of nanostructures with varying morphologies and functions. From simple micelles and vesicles to more complex superstructures, ISA provides a versatile platform for designing materials with specific properties for diverse applications. This is why ISA is considered a powerful tool for developing functional materials with broad potential uses.[36]

2. What is nanoarchitectonics?

Nanoarchitectonics is a multidisciplinary concept that involves the design and construction of functional materials and systems at the nanoscale.[37] It integrates elements from nanotechnology, materials science, chemistry, physics, and biology to create complex structures with precise control over their properties and functions.[38] The term "nanoarchitectonics" was introduced in the early 2000s by Masakazu Aono and his colleagues.[3940] Aono, a pioneering scientist in nanotechnology, emphasized the need for a new paradigm that would enable the construction of highly sophisticated nanostructures with tailored functionalities. Within this paradigm, Katsuhiko Ariga has been one of the most prominent advocates of this discipline, popularizing the term "nanoarchitectonics" across various fields of knowledge.[41]

The term "nanoarchitectonics" is derived from "nano," referring to nanometer-scale dimensions (1 to 100 nanometers), and "architectonics," which pertains to the design and construction of structures. Essentially, nanoarchitectonics focuses on the rational design of materials, systems, and devices by assembling nanoscale building blocks (such as molecules, nanoparticles, or nanostructures) in a controlled and purposeful manner.[42] This concept emerged as a natural evolution of several scientific fields as our understanding of nanoscale phenomena expanded and evolved, highlighting both the need and the opportunity to create more sophisticated materials and devices.[43]

Nanoarchitectonics is a transformative approach in materials science with the clear goal of constructing functional systems and devices from nanoscale components. In this context, there is a critical need to regulate, control, and modulate structures at the nanoscale to enhance material performance. While traditional fields such as organic synthesis, polymer chemistry, and materials science contribute significantly to the creation of functional materials, nanoarchitectonics offers an alternative and complementary perspective, emphasizing precise control at the atomic and molecular levels. By merging principles from nanotechnology with disciplines like organic chemistry, supramolecular chemistry, materials science, and biotechnology, nanoarchitectonics aims to engineer materials with advanced functionalities. In nanoarchitectonics, structural formations and transformations start with individual atoms and molecules, evolving into organized, functional materials. This process enables the design of materials with properties tailored to specific applications.

3. Why Ionic Self-Assembly (ISA) is a Good Match for Nanoarchitectonics

Ionic self-assembly (ISA) is a powerful and versatile strategy that aligns exceptionally well with the principles of nanoarchitectonics for several compelling reasons, which are detailed below:

Precision in structural control: ISA relies on electrostatic interactions between oppositely charged molecules, which are highly directional and predictable, allowing for the controlled assembly of complex structures at the nanoscale.[44,45] This precision is one of the fundamental requirements of nanoarchitectonics, which aims to create precise and functional nanostructures by organizing materials at the atomic or molecular level.[46,47] The "molecular" precision offered by ISA fulfills this requirement, enabling the design of well-defined nanostructures with specific properties.[48,49]

Versatility in material selection: One of the standout features of ISA is its flexibility in material usage. A wide range of charged molecules, such as surfactants, polyelectrolytes, and even lipids, can participate in ionic self-assembly.[50] This versatility allows for the incorporation of various functional components into the assembled structure.[51] This characteristic of ISA aligns with a primary necessity of nanoarchitectonics, which is the ability to integrate diverse materials into a single, complex nano- mesostructure.[52,53] In this regard, ISA provides the material flexibility needed to achieve this goal, making it an ideal tool for constructing complex nanoarchitectonic systems.[54]

Scalability and processability: ISA processes are typically straightforward and can be performed under mild conditions, making them suitable for large-scale production and practical applications. The process of forming polyelectrolyte-surfactant complexes can be adapted to various scales, from laboratory to industrial production. Methods such as spin-coating, dip-coating, or spray-coating can be used to apply these complexes to surfaces.[55] The materials used in these complexes are often cost-effective, and the ability to form complexes in aqueous solutions can simplify the manufacturing process and reduce costs. This is a particularly valued trait because, for nanoarchitectonics to be applied in real-world scenarios, the methods used must be scalable and cost-effective.[56] ISA meets these criteria, facilitating the transition from laboratory research to industrial applications.[57]

4. Design and Synthesis of Materials through Ionic Self-Assembly

The design and synthesis of materials via ionic self-assembly (ISA) involve several critical steps, including the selection of charged building blocks, the choice of synthetic or preparative methodologies, and the control of assembly conditions. Each of these factors plays a pivotal role in determining the properties and functionality of the resulting material.

Selection of Charged Building Blocks: The choice of building blocks is a crucial aspect of the ISA process. These building blocks typically consist of charged surfactants, polyelectrolytes, and other charged molecules that can engage in electrostatic interactions. The selection of these components is guided by the desired properties of the final material,[58] such as size, shape, mesostructure, and surface chemistry.

The nature of the surfactant directly influences the effectiveness of the ISA technique. The hydrophobic tails of surfactants can form micelles or vesicles, while the charged head groups interact with oppositely charged species to drive self-assembly.[59] The intensity of the interaction between the charged head of the surfactant and the charged monomers of the polymer significantly affects the viability of this method for achieving the desired mesostructures.[60] Therefore, the choice of surfactant can profoundly impact the morphology of the final material,[61] with different surfactants leading to the formation of distinct structures, such as lamellae, hexagonal phases, or cubic phases.[62,63]

Similarly, polyelectrolytes are another essential component in ISA. Polyelectrolytes can interact with oppositely charged surfactants or small molecules to form complex coacervates, layer-by-layer assemblies, or other organized structures. The length, charge density, and flexibility of the polyelectrolyte can be tailored to control the properties of the assembled material, including its mechanical strength, porosity, the dimensional characteristics of hydrophilic domains, and responsiveness to environmental stimuli.[64,65]

Synthetic and Preparative Methodologies: Several synthetic methodologies can be employed to carry out ionic self-assembly (ISA), each offering distinct advantages and challenges.[66] One of the simplest methods is stoichiometric precipitation, where the charged components are mixed in stoichiometric amounts to form a precipitate. These stoichiometric polyelectrolyte-surfactant complexes resemble comb-shaped polymers, where each polymer chain unit bears an electrostatically bound “side chain.” These complexes are typically insoluble in water but, in many cases, are soluble in diverse organic solvents. While this method is straightforward and efficient, controlling the size and morphology of the resulting material can be challenging. In the case of nonstoichiometric complexes, they are generally formed by using an excess of either polyelectrolyte or surfactant, leading to the generation of structures typically described as micellar aggregates surrounded by polyelectrolyte chains.

Another common technique is solvent evaporation, where the charged components are dissolved in a solvent and then allowed to evaporate, leading to the self-assembly of the material.[67] This strategy is similar to the evaporation-induced self-assembly (EISA) method.[68,69] Solvent evaporation offers better control over the assembly process, as the evaporation rate can be adjusted to influence the final structure. However, achieving reproducible results requires careful control of the solvent composition and evaporation conditions.[70,71]

Layer-by-layer (LbL) assembly is a more sophisticated method that involves the sequential deposition of charged layers onto a substrate.[72,73] The combination of LbL techniques with polyelectrolyte-surfactant complexes opens up new opportunities for creating interfacial assemblies with tunable mesostructural features. This has significant implications, as the structural complexity induced by organized mesoscopic domains can define the functional properties of the film.[74] Through this approach, well-defined film mesostructures with tailored spatial configurations have been obtained, which are crucial for applications requiring vectorial transfer of energy, electrons, or matter.[75,76] Implementing an LbL strategy allows for precise control over the film thickness, composition, and organization as micellar structures and polyelectrolytes are incorporated into the film. However, it should be noted that achieving better control over film thickness does not necessarily imply a linear relationship between the number of layers and thickness. In fact, it has been reported that in the assembly of CTAB with PAA, the films grow supralinearly, regardless of the molecular weight of the polyelectrolyte used.[77] One disadvantage of this approach is that it is a time-consuming process requiring careful optimization of the deposition conditions.

Control of film properties and morphology through the assembly solvent: The nature of the solvent plays a crucial role in ionic self-assembly (ISA), significantly influencing both the process and the properties of the resulting materials.[78] Solvent polarity determines the strength and nature of the electrostatic interactions between the charged components.[79] In polar solvents, such as water, ionic species are more solvated, which can weaken the electrostatic attractions between oppositely charged molecules. Conversely, in less polar or non-polar solvents, these interactions can be stronger, promoting a more compact assembly of the ionic components. The interactions between the solvent molecules and the charged building blocks (e.g., surfactants, polyelectrolytes) affect the solubility and aggregation behavior of these components. For instance, a good solvent will dissolve the components effectively, potentially leading to more uniform self-assembly. On the other hand, a poor solvent may induce aggregation or precipitation, influencing the morphology and structure of the assembled material.[80] This phenomenon is quite common in ISA, and while it may be viewed as a disadvantage from one perspective, it is indeed advantageous because it allows manipulation of the structural richness of the films through the simple choice of solvent or even by using co-solvent mixtures.[81] Hence, the presence of co-solvents can be employed to fine-tune the self-assembly process. For example, adding a small amount of a non-polar solvent to a polar solvent can reduce the solvation of the ionic species, thereby enhancing their interactions and altering the self-assembly process. As previously mentioned, in methods such as solvent evaporation-induced self-assembly (EISA), the rate of solvent evaporation directly impacts the kinetics of self-assembly.[82] A slower evaporation rate provides more time for the components to self-organize into well-ordered structures, whereas a faster rate may result in less controlled, kinetically trapped assemblies. In this context, it is reasonable to assume that the solvent viscosity also affects the self-assembly process; an increase in viscosity slows down the diffusion processes, which could lead to changes in the self-assembly dynamics and affect the complexity of the resulting structure.[83] Moreover, solvent quality can induce changes in the conformation of polyelectrolytes or surfactants. For instance, assemblies generated in aqueous environments lead to the formation of films with hydrophilic characteristics, while the same surfactant-polyelectrolyte pair assembled from an organic solvent results in hydrophobic films. Thus, careful selection and control of the solvent are critical for achieving the desired material properties in ISA and change its properties over time.

5. Bioelectrochemical systems via “ionic self-assembly + nanoarchitectonics”

Bioelectrochemistry is an interdisciplinary field that combines principles from biology, chemistry, and electrochemistry to study and manipulate the interactions between biological systems and electrical currents or potentials. It explores how biological molecules, such as enzymes, interact with electrodes and how these interactions can be applied to biosensors, medical diagnostics, and other technologies.[84] In this context, ionic self-assembly (ISA) and nanoarchitectonics play a critical role in advancing bioelectrochemistry by creating functional, complex interfaces that enhance the interaction between biological molecules and electrodes. ISA organizes oppositely charged molecules into well-defined structures through electrostatic interactions, generating interfaces that improve enzyme stability and activity when integrated into electrochemical devices.

Enzyme immobilization is essential in electrochemistry and bioelectrochemistry for developing biosensors and bioelectrodes with enhanced performance.[85,86] Polyelectrolyte-surfactant complexes provide a unique environment for enzyme immobilization, which can enhance their biological activity. The strength and nature of the interaction between the enzyme and the complex can be precisely adjusted by varying the types and ratios of polyelectrolytes and surfactants.[87-89] This flexibility enables the design of tailored immobilization processes that improve the stability and performance of biosensors.[90]

Furthermore, ISA can enhance electron transfer between biological molecules and electrodes, a critical factor for applications such as biosensors, where efficient electron transfer directly impacts sensitivity and detection limits. Designing ISA systems with built-in redox functions offers several advantages, as it eliminates the need for external redox mediators.[91-93] This reduction in system complexity improves the overall efficiency of electron transfer, which is essential for high-performance bioelectrochemical devices like biosensors and biofuel cells. Additionally, built-in redox functions contribute to the amplification of electrochemical signals resulting from molecular recognition processes.

On the other hand, nanoarchitectonics involves the deliberate construction of complex, hierarchical nanostructures with precise control over their properties. In bioelectrochemistry, this approach facilitates the development of highly tailored interfaces that optimize interactions between biological molecules and electrodes, thus enhancing the performance of bioelectrochemical devices. Nanoarchitectonics also allows for the integration of multiple functional components, such as nanomaterials (e.g.: metal nanoparticles, carbon nanotubes), enzymes, and redox mediators, into a single cohesive structure. This multifunctionality results in more efficient bioelectrochemical systems, including biosensors with improved sensitivity and biofuel cells with enhanced energy output.[94]

6. Redox-active polyelectrolyte-surfactant complexes: supramolecular materials with built-in electroactive chemical functions.

6.1. Electroactive assemblies of polyelectrolytes and surfactants with ferrocene and viologen redox centers.

The use of ferrocene as a redox center in electroactive materials presents both advantages and disadvantages, depending on the specific context in which it is applied, such as in biosensors, catalytic systems, or energy storage devices. Among its key advantages are its excellent redox reversibility, which is critical for applications in electrochemical sensors and energy storage devices. Ferrocene can be incorporated into polymers and amphiphilic molecules through relatively straightforward synthetic protocols, enabling the creation of diverse molecular architectures. This flexibility broadens its applicability in electroactive systems. Its moderate redox potential makes it particularly suitable for a wide range of systems, including bioelectrochemical applications, facilitating efficient electron transfer without the need for high applied voltages, thereby minimizing the risk of undesirable side reactions.

However, it is important to note that under extreme oxidation conditions or in highly aggressive media, ferrocene can undergo irreversible oxidation, which would compromise its redox reversibility. One of the earliest attempts to produce mesomorphic electroactive materials using redox-active polyelectrolyte-surfactant complexes was reported by Tong et al.[95] These materials were created through ionic self-assembly of sodium poly(styrenesulfonate) (PSS) and ferrocenyl surfactants based on *n*-alkyl (ferrocenylmethyl)ammonium bromide (Fcn, $n = 8$, 12, 16, where n refers to the carbon number of the alkyl chain) in solution.

The resulting materials were characterized using multiple techniques, revealing the significant influence of the alkyl chain length on the properties of the synthesized materials. These materials exhibited lamellar organization with interlamellar spacings (d) of 2.49, 2.94, and 3.74 nm for PSS-Fc8, PSS-Fc12, and PSS-Fc16, respectively. In terms of thermal stability, it was observed that the assembled materials displayed greater thermal stability than their individual components (surfactant and polyelectrolyte), which was attributed to the strong electrostatic interactions between the sulfonate groups and quaternary ammoniums. Cyclic voltammetric characterization demonstrated that the redox reversibility of these electrochemical processes was affected by the alkyl chain length, with the redox reversibility diminishing as PSS-Fc8 was replaced by PSS-Fc12 or PSS-Fc16 in the assemblies (**Figure 1**). This effect on charge transfer processes was evidenced by the increase in peak-to-peak separation (ΔE) observed in the cyclic voltammetry of the different assemblies. The self-assembled materials with longer surfactant tails exhibited less reversible redox behavior due to their higher ΔE values. A similar approach was later reported by Li and Li,[96] where instead of using PSS, they employed sodium polyacrylate. As in the previous case, the resulting complexes exhibited a crystalline and lamellar mesomorphous structure. Moreover, the reversibility of the electrode process deteriorated as the surfactant tail length increased, due to the more ordered packing in the complex film formed by longer surfactant tails.

The ability to manipulate the topology of molecules involved in ionic self-assembly significantly expands the range of electroactive mesostructures that can be obtained through this straightforward and direct synthetic process. For instance, the assembly of poly(ferrocenylsilane) and dendritic amphiphiles has enabled the creation of thermotropic liquid crystalline redox-active materials.[97] It has been demonstrated that the combination of cationic linear poly(ferrocenylsilane) (PFS) with anionic dendrons of 3,4,5-tris(n-alkan-1-yloxy)benzoic acid [(3,4,5)*n*G1 COOK, where $n = 12$, 14, 16, representing the number of carbon atoms in the alkyl tail, leads to the formation of crystalline phases in the resulting complexes (**Figure 2**). Samples prepared by dropcasting from chloroform solutions showed that these dendritic amphiphiles form an end-to-end bilayer lamellar structure, with long periods of $d = 4.84$, 5.34, and 5.76 nm for n = 12, 14, and 16, respectively. It has been observed that as the amphiphilic chain length increases, the organization of lamellar domains improves. Despite the structural complexity of the building blocks in these assemblies, the materials exhibit excellent electrochemical reversibility. This finding underscores the potential of these sophisticated assemblies for applications requiring highly ordered, redox-active materials with tunable structural properties.

The use of polyferrocenylsilane (PFS) as a cationic polyelectrolyte building block in ionic assemblies has also been extended to its combination with bis-2-ethylhexyl sulfosuccinate (AOT) and an azobenzene surfactant (azoB12) as amphiphilic components.[98] X-ray characterization of these assemblies prepared by dropcasting from chloroform solutions revealed the presence of materials organized at the mesoscale. It was observed that the nature of the surfactant did not significantly influence the lamellar spacing of the mesomorphic nanostructures. However, further characterization indicated that, compared to PFS-AOT assemblies, the PFS-azoB12 complexes formed materials with greater lamellar order at the microstructural level. This enhanced order was attributed to the rigid nature of the azobenzene moiety and the π-π interactions that likely promoted the formation of more ordered lamellar mesophases. These findings highlight the impact of specific molecular interactions on the structural organization of ionic assemblies, offering valuable insights into the design of highly ordered electroactive materials for advanced functional applications. The choice of surfactant and polyelectrolyte, in terms of both their architecture and function, played a key role in enabling the design of complexes with different mesomorphic states. A notable example of this is the use of block copolymers of polyferrocenylsilane in combination with AOT and perfluorinated AOT, which led to the formation of various hierarchically organized mesostructured materials.[99]

In this context, Manners and co-workers explored the ionic assembly of polystyrene-b-poly(ferrocenylmethyl(dimethylaminopropynylsilane)) (PS-b-PFAMS) diblock copolymers in combination with sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and sodium bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl) sulfosuccinate (AOTF) (**Figure 3**). One of the most remarkable aspects of this work is the role played by the predominant interactions and the chemical identity of the surfactant in determining the mesostructures obtained. The complexation of PS-b-PFAMS with 9-AOT resulted in distorted lamellar morphologies, as evidenced by transmission electron microscopy (TEM) observations. Small-angle X-ray scattering (SAXS) analysis of these materials revealed a broad first-order reflection at $q = 0.22\ \text{nm}^{-1}$, corresponding to a d-spacing of 29 nm, along with additional weak reflections (**Figure 4**). These samples were prepared by drop-casting several layers of concentrated solution of the material from toluene to form a thick film on a solid substrate.

When these results were compared with the complexation of PS-b-PFAMS and the perfluorinated AOT, significant differences were found. In this case, well-defined polystyrene cylinders were observed within a PFAMS-surfactant matrix, with average periodicities of 35 nm. It is plausible that the highly hydrophobic fluorocarbon groups promote a more pronounced phase segregation, resulting in sharper phase boundaries at the interface between the functional domains. A further distinction revealed by SAXS was that the reflections observed at the block copolymer length scale were consistent with those of a hexagonal phase. Additionally, the scattering vector at larger q values depicted a broad reflection at $q = 2.6\ \text{nm}^{-1}$ ($d = 2.4$ nm), indicative of ordering at the polymer-surfactant length scale as a result of ionic self-assembly (ISA). SAXS, combined with TEM and atomic force microscopy (AFM) characterization, clearly demonstrated that the sample exhibited hierarchical organization at two distinct length scales (**Figure 5**).

The influence of the chemical identity and topological characteristics of the surfactant on the morphology of ionic assemblies based on redox-active polyferrocenylsilane has been detailed in a series of elegant experiments, where the nature of AOT was varied to give rise to a range of morphologies that are challenging to achieve using block copolymers alone.[100] Notably, it was found that the volume and architecture of the alkyl tail play a crucial role in the formation of non-trivial morphologies. It is hypothesized that packing constraints can lead to shifts in morphology from the expected lamellar structures to other unexpected arrangements, such as the tetragonal organization observed in the assembly of polyferrocenylsilane with AOT functionalized with phenyl groups. These findings underscore the critical role of surfactant chemistry in tailoring the structural organization and functionality of ionic assemblies, paving the way for designing materials with hierarchical order for advanced applications.

In line with this conceptual framework, Manners, Faul, and co-workers[101] employed the ionic self-assembly (ISA) approach to construct supramolecular materials incorporating both redox and photoactive functionalities. **Figure 6** illustrates the structure of PFS-based diblock copolymers ionically complexed with ethyl orange (EO) chromophores. This material is referred to as PFEMS112-b-PFAMS(EO)112 (PFEMS = poly(ferrocenylethylmethylsilane), PFAMS = poly(ferrocenylaminomethylsilane)). TEM characterization reveals that the material adopts a cylindrical morphology with periodicities of 28 nm, extending several microns in length throughout the material. The higher electron density of the PFEMS blocks compared to the PFAMS(EO) blocks facilitates the identification of the domains occupied by each building block, revealing that the material exhibits a local liquid crystalline order characterized by cylindrical morphologies. This type of approach could be highly valuable for the development of supramolecular materials with combined functionalities integrated within hierarchical structures, opening new avenues for advanced material design.

As previously mentioned, the formation of polyelectrolyte-surfactant assemblies can typically be achieved through direct combination; however, this is not the only strategy that leads to mesoorganized and electroactive films. An alternative approach involves the layer-by-layer (LbL) deposition of polyelectrolytes and surfactants, thereby constructing ionic assemblies sequentially on a substrate.

When considering both approaches, it is evident that, from a preparative perspective, each method has its advantages and disadvantages. Direct ionic assembly is characterized by its simplicity and speed in sample preparation, as it relies on electrostatic interactions between charged components, facilitating rapid structural formation. Generally, this technique allows for the generation of less compact structures, often exhibiting greater surface roughness and heterogeneity. Consequently, the formation of supramolecular materials via direct ionic assembly may present limitations - compared to layer-by-layer assembly - when it comes to controlling the morphology and thickness of the resulting films. Additionally, depending on the nature of the building blocks, achieving uniform and well-defined layers using direct ionic self-assembly can be challenging, particularly in complex structures.

On the other hand, the layer-by-layer assembly of polyelectrolytes and surfactants is inherently a slower preparative process due to the necessity of depositing each layer individually. Nonetheless, despite this inevitable limitation, LbL assembly offers several advantages that may be attractive depending on the desired sample characteristics.[102] This method allows for precise control over the thickness and composition of each layer, enabling the incorporation of functional features with greater spatial precision within the nanostructure. Consequently, different materials can be integrated into alternating layers, facilitating the creation of materials with specific functional properties within a predefined organization, dictated by the characteristics of the surfactants acting as structure-directing agents.

This LbL ionic assembly approach using polyelectrolytes and surfactants has been extensively explored by Piccinini and co-workers[103] through the assembly of polyacrylic acid (PAA) and (ferrocenylmethyl)hexadecyldimethylammonium bromide (FcCDAB). These authors demonstrated that the layer-by-layer assembly of redox surfactants and polyelectrolytes can lead to the formation of organized electroactive films at the mesoscale, where the mesoorganization could be modified through the combined use of different surfactants. Their findings showed that the incorporation of ferrocene-appended surfactants into LbL films results in superlattice-like supramolecular arrays, with mesostructures ranging from circular hexagonal to 2D hexagonal configurations, depending on the content of the redox amphiphile within the assembly. This strategy of co-assembling an electroactive surfactant with a non-electroactive counterpart has been employed to regulate the concentration of functional units within the film.

In **Figure 7,** GISAXS patterns of $(PAA/surfactants)_7$ assemblies prepared from solutions with varying CTA ratios are presented, illustrating that the mesostructure evolves from a circular hexagonal phase to a 2D hexagonal phase with increasing content of the electroactive surfactant in the assembly. **Figure 8a** presents the voltammograms of mesostructured $(PAA/surfactant)_5$ assemblies (**Fig. 8b, left**) prepared on gold electrodes. It is evident that an increase in the proportion of redox surfactant significantly enhances the faradaic current, attributable to the augmented presence of ferrocene centers within the film. However, it has also been experimentally observed that excessive increments in the redox surfactant concentration (i.e. higher than 60%) can result in greater instability of the film. As ferrocene undergoes oxidation, a high density of positive charges is generated inside the film causing gradual desorption, probably due to electrostatic repulsions between the components. Nevertheless, it has been confirmed[104] that in the case of $(PAA/CTA_{0.5}\text{-}FcCDA_{0.5})_7/PAA$ assemblies, where the ferrocene content constituted approximately 50% of the maximum nominal value of ferrocene within the mesostructure, the film exhibits remarkable stability, demonstrating a highly reversible electrochemical response indicating good connectivity between the ferrocene redox centers and the electrode.

These authors also studied the hydration of the (PAA/CTA-FcCDA) films and demonstrated that the film absorbed meager amounts of water, less than 15%, while assemblies made of polyanions and polycations normally hydrate between 30-70%.[105-106] Furthermore, the mass and charge transport studied by E-QCM (**Fig. 8b, right)**) demonstrated that the ingress (egress) of the counter ions during the electrochemical oxidation (reduction) is accompanied by a small amount of water, which is close to the ion hydration sphere. Thus, $(PAA/CTA_{0.5}\text{-}FcCDA_{0.5})$ mesostructured films have an efficient charge transport with negligible changes in their meso-organization during the electron transfer process.

For this reason, it is crucial to highlight that the choice between direct ionic assembly and polyelectrolyte-surfactant layer-by-layer assembly will depend on the specific requirements of the application, including material stability, the need for structural control, and desired functional properties.

Viologens are a family of molecules related to 1,1'-dialkyl-4,4'-bipyridine, which have long been used in electrochemical applications due to their ability to undergo reversible redox processes.[107-109] The use of viologens as redox functional units has been facilitated by the development of various preparative methods, particularly the Menshutkin reaction of 4,4'-bipyridine with alkyl halides, leading to a wide variety of viologen-based functional molecules and polymers.[110-113] One of the earliest works on the preparation of electroactive materials based on polyelectrolyte-surfactant complexes containing viologens as redox centers was presented by Okahata and En-na in the late 1980s.[114] These authors explored the integration of viologen groups either in the polyelectrolyte or in the surfactant to construct "soft" membranes (**Figure 9**) whose transport properties could be electrochemically controlled in combination with temperature. Cross-sectional TEM characterization (**Figure 10**) of these films revealed a well-defined multilayer structure whose mean thickness is ~ 4 nm. The use of electrochemical redox reactions facilitated the control of permeation in mesoorganized membranes ($2C_{16}V^{2+}/PSS^-$) prepared from an aqueous dispersion of $2C_{16}V^{2+}ClO_4^-$ amphiphiles and an aqueous solution of sodium polystyrene sulfonate (PSS). This mixing process was carried out at 70°C, a temperature at which the bilayer-forming amphiphiles are in a crystalline state above their transition temperature. The precipitates were washed and purified by reprecipitation in chloroform with methanol. The studies were conducted by forming a film on a Pt minigrid electrode to study the diffusion through the membranes under different potential and temperature conditions. Experimental data showed that the electrochemical reduction of the viologen units from their dicationic to radical cationic form raised the phase transition temperature (Tc) of the bilayers from 24°C to 38°C. Therefore, at 30°C, the permeability of the oxidized form $2C_{16}V^{2+}/PSS^-$ is higher due to the fluidity of the liquid crystalline state, considering that the transition temperature for the $2C_{16}V^{2+}$ bilayers is 24°C. Similarly, permeability decreases when the film is reduced, as the bilayers of $2C_{16}V^{+\cdot}$ have a transition temperature of 38°C, meaning that at 30°C they are in a solid state.

On the other hand, in the case of the $2C_{12}SO_3^-/polyV^{2+}$ assemblies, the permeation of the prepared films was not affected by the redox changes, even over a wide temperature range. The electrochemical changes could be visualized through color variations in the complexes, indicating that the polyelectrolyte-surfactant complexes underwent redox transitions at different temperatures. The redox response and the absence of changes in permeability led to the conclusion that the redox reaction of viologens, localized in the polyelectrolyte-rich hydrophilic region and not near the alkyl bilayer, does not contribute to permeability modulation by the redox state of the viologen units.

6.2. Redox-active polyelectrolye-surfactant assemblies integrating conducting polymers.

Polyaniline (PANI), a widely studied conducting polymer, has garnered attention over the past decades due to its unique electrochemical properties, making it a key material in applications related to energy storage devices, sensors, and actuators.[115-118] Its molecular structure allows it to exhibit multiple oxidation states, enabling it to function as a redox polymer. This reversible electron transfer capability is particularly useful in systems that require controlled redox reactions, such as electrochemical biosensors.[119] Conducting polymers like polyaniline and polypyrrole are often considered "redox polyelectrolytes" due to their macromolecular structure, the ability to incorporate ionizable groups, and their remarkable redox activity, which is intrinsically tied to their electroactivity.[120]

Contrary to redox polymers where redox units are grafted onto the polyelectrolyte backbone, in conducting polymers, the electroactive units form part of the polymer main chain.[121] These polymers possess active redox sites along their chains, meaning they can accept or donate electrons, altering their oxidation state. This redox process is fundamental to their electrical conductivity, as it facilitates the movement of electrons or protons through the material. Unlike conventional polyelectrolytes, whose main role is the mobility of ions in solution, conducting polymers not only interact with ions but also actively participate in electron transfer. This electron exchange differentiates them as "redox polyelectrolytes," as their electroactive properties are not solely dependent on dissolved ions but on their capacity to engage in redox reactions directly.

For a long time, and even today, there is significant interest in using and applying polyaniline as a conducting/redox polymer. This interest is rooted in three key factors: the monomer (aniline) is relatively inexpensive, the polymerization process is straightforward, and the polymerization reaction yields high efficiency. Polyaniline was initially considered difficult to process, but the ability to be doped with protic acids has greatly improved its solubility and processability. Polyaniline in its emeraldine base (EB) form can be treated with an acid, leading to a charge redistribution that generates a radical cation charge carrier in the conductive emeraldine salt (ES) state. One of the first researchers to investigate the processability of PANI was Alan Heeger and his team in 1992.[122] They demonstrated that by using the appropriate protic acid to protonate PANI, it was possible to enhance its processability, developing strategies to manipulate and process conductive PANI using specific counterions.

It is well known that starting from the insulating emeraldine base form, polyaniline can be converted into a conducting state through two independent doping routes: (i) oxidation, either electrochemically or chemically, and (ii) protonation through acid-base chemistry by exposure to protic acids (for example, in an aqueous environment with a pH of less than 2-3). It is important to note that these two routes can lead to different final states. Exploring the second doping route revealed that surfactants, such as dodecylbenzenesulfonic acid (DBSA), can promote the solubility of the PANI-DBSA complex in various solvents, including toluene, xylene, and chloroform. This finding, as reported by Heeger and co-workers,[123] has been seminal because it opened the door to the notion that with the appropriate choice of functionalized protic acid (surfactant), polyaniline can be made soluble in a variety of common organic solvents.

Other authors have demonstrated that the use of plasticizing surfactants can induce self-organization in the structure of PANI, with subsequent effects on the structure-function relationship of the material.[124,125,126] Studies on processable and conducting polyaniline complexes, including sulfonic acid-based surfactants, have led to the notion that the conductivity and "crystalline" structure of polyaniline protonated with dodecylbenzenesulfonic acid are proportional to the molar concentration of the acid dopant. Protonation leads to a layered structure, as evidenced in X-ray diffraction patterns, and the degree of crystallinity increases in a manner similar to the conductivity as a function of acid concentration.

The effect of dodecylbenzenesulfonic acid on the mesoorganization of PANI-DBSA complexes was studied in detail by Levon and co-workers[127,128] in the mid-1990s. **Figure 11** shows the X-ray patterns for the complexes with various PANI-DBSA ratios. Before measurement, the samples were treated at 100°C for 20 minutes. All X-ray data for the complexes reveal the presence of a layered structure. For complexes with a PANI ratio of 1:1 and 1:2, the *d*-spacing is 3 nm, attributed to the interlayer distance. This value slightly contracts (to 2.7–2.8 nm) as the PANI ratio increases to 1:3, 1:4, and 1:5. This tendency of polyaniline to form layered structures is attributed to the inherent rigidity of the polymer main chain. Furthermore, the complexation of the polyaniline chains with surfactants further stiffens the complex structure, even inducing liquid crystallinity in the material.[129] The layering effect of PANI-surfactant complexes is also observed in layered neutral alkylated polyanilines, where the interaction between the alkyl side chains of the PANI backbone and the long alkyl tails of DBSA facilitates the formation of well-defined layered structures.[130] In such cases, it has been observed that the interlayer distance (*d*) is determined by the length of the side chains or the surfactant dimension, without a decrease in interdigitation.

These structural properties observed in such solid-state systems are primarily due to the dopant (surfactant)–polymer chain interactions. In fact, an idealized structure of PANI doped with surfactants can be interpreted as a macromolecular comb-like system (**Figure 12**), where the anionic surfactants represent the pendant side groups attached to every second nitrogen of the polymer chain. In these systems, the interdigitation between the surfactant chains provides a notable stabilizing factor, as inferred from experimental measurements and molecular dynamics simulations.[131]

As an alternative to using high molecular weight polyaniline, which suffers from low solubility and limited processability, working with oligomeric PANI has been proposed to facilitate the manipulation of these materials. Faul and co-workers have demonstrated that it is possible to synthesize monodisperse and highly soluble PANI oligomers with well-defined structures and molecular characteristics.[132] These authors prepared thin films of aniline tetramer (TANI) and octamer (OANI), both in their native emeraldine base (EB) oxidation state and in the doped emeraldine salt (ES) state, complexed with the acid surfactant bis(ethyl hexyl)phosphate (BEHP) (**Figure 13**).

The films were prepared via simple drop-casting and solvent annealing processes and characterized using X-ray techniques. Structural characterization revealed that the presence of the BEHP surfactant promoted the self-organization of the material, leading to highly ordered structures (see **Figure 14).** Grazing-incidence X-ray scattering (GIXS) also showed that the morphology, orientation relative to the underlying substrate, and the degree of orientation depended on the molecular architecture of the oligomer. While the BEHP-TANI system formed highly oriented hexagonal units, the BEHP-OANI system exhibited a randomly oriented lamellar structure with a *d*-spacing of 2.25 nm. This detailed structural characterization provided relevant insights beyond mere structural analysis. In this case, the significance of the results lies in the experimental observation that the assembly and organization of oligomer–BEHP complexes in thin-film configurations differ from those observed in bulk-phase materials. Another interesting aspect of these findings is that through a simple processing route, the morphology of electroactive oligomer films can be tailored by slight changes in the molecular dimensions or repeating units of the oligomer.

Another interesting strategy to improve the processability of PANI and promote the formation of PANI-surfactant complexes involves modifying the aniline monomer to incorporate amino groups into each monomeric unit. The synthesis of these PANI-derived polymers was reported by Marmisollé and co-workers using oxidative polymerization of 3-aminobenzylamine (PABA) as the preparative method. They demonstrated that the polymers synthesized in this way significantly enhanced their processability in aqueous solutions.[133] This type of conducting polymer, PABA, also exhibits superior electroactivity in neutral solutions compared to PANI.[134,135] Additionally, the specific interaction between protonated amines and phosphate anions provides a fertile platform for constructing supramolecular materials via self-assembly processes.[136-142] Due to the strength of hydrogen bonding, phosphate anions interact much more strongly with charged amines than other similar divalent anions.[143-146] This association results in a higher protonation degree of the amines and a higher dissociation degree of phosphates.[147,148]

In this context, Lorenzo *et al.*[149] proposed a strategy to obtain electroactive films through the complexation/assembly of polyaminobenzylamines (PABA) and sodium monododecyl phosphate (DP). They demonstrated that the self-assembly of these two components led to the formation of well-defined lamellar structures, which showed good electroactivity in neutral solutions. From XPS measurements of PABA-DP films, it was inferred that the proportion of positively charged quinone-like moieties increases compared to PABA alone, suggesting that the interaction with DP stabilizes this oxidized form. Furthermore, the anionic surfactant may act as a dopant, enhancing the electroactivity of the material.[150]

Supramolecular PABA-DP films with varying compositions can be prepared by mixing PABA and DP solutions in different proportions. The mixing process consistently generates a precipitate, which is separated from the supernatant by centrifugation. The solid material is then dissolved in DMF and spin-coated onto gold electrodes for thin-film assembly. The procedure for film preparation is illustrated in **Figure 15.**

X-ray reflectivity (XRR) characterization of PABA–DP samples with a 1:5 PABA-DP ratio revealed well-defined, equally spaced Bragg peaks in the reflectogram, confirming the presence of highly oriented lamellar structures **(Figure 16).** From the Bragg peak positions of the PABA–DP films with different PABA ratios - 1:2, 1:5, and 1:10 - lamellar spacings (*d*) of 3.58, 3.55, and 3.59 nm were estimated, respectively. Additionally, GISAXS patterns obtained for the PABA-DP films showed intense bright spots along the q_z direction, indicating the presence of lamellar structures predominantly oriented parallel to the substrate.

Figure 17 presents the voltammograms of a PABA–DP-coated gold electrode in an acidic solution. The electrochemical response shows a main redox couple at ~0.43 V, which is in excellent agreement with values reported in the literature.[134] Notably, higher currents were measured for films with a lower sodium monododecyl phosphate content in the assembly solution. However, regardless of the surfactant content in the film, potential cycling resulted in a stable electrochemical response in all cases, suggesting that PABA domains remain electroactive within the assemblies.

It is important to note that electron transfer across the films requires both electron propagation and ionic transport to maintain local electroneutrality. Thus, despite the intrinsic rigidity and hydrophobicity of these films, it is plausible to infer that they do not hinder ionic transport within the mesostructure. In this sense, the lamellar organization should not be seen as infinite layers covering the entire electrode surface, but rather as lamellar microdomains. Imperfections at the boundaries of these domains likely create pathways connecting different PABA regions, thereby maintaining the conductive properties of the mesostructured films. Regarding charge compensation during the redox process, proton mobility appears to be the predominant mechanism, rather than anion ingress and egress, during potential scans. These results highlight the versatility and utility of ISA films based on polyaminobenzylamines (PABA) and sodium monododecyl phosphate (DP) complexes. The combination of specific amine-phosphate supramolecular interactions and the structural driving force of polyelectrolyte–surfactant complexation can lead to the production of films with well-defined lamellar structures and good electroactivity in neutral solutions.

Polypyrrole (PPy) is another conductive polymer that has also been widely used in conjunction with surfactants as modulators of its mesostructure. In this context, it is important to highlight a seminal work by Wegner and collaborators[151] on the synthesis of polypyrrole with layered structures via formation of complexes with *n*-alkylsulfates and *n*-alkylsulfonates. These authors found that when polypyrrole was electrochemically synthesized in the presence of surfactants, XRD characterization revealed the presence of Bragg peaks, indicating the mesoorganization of the electrosynthesized material. When the synthesis was performed with surfactants of different chain lengths (*n*), a linear correlation was observed between the lamellar spacing of the PPy-alkylsulfonate complex and the chain length (**Figure 18**).

The electrochemical behavior of these materials was extensively studied by De Paoli et al.[152,153] who observed that the redox behavior of PPy is largely influenced by the nature of the anionic surfactant. The assembly and intercalation of dodecyl sulfate anions within the PPy matrix is largely responsible for the high stability of the polymer under repeated voltammetric experiments. Despite the apparent rigidity of the mesostructure observed in PPy-DS systems, the electrochemical behavior shows a highly reversible response within the potential range where at least two redox processes occur. Furthermore, when these samples were tested in EQCM experiments, two notable features were observed. First, at the onset of the oxidation process, only cation expulsion occurs, while anion expulsion begins with the start of the reduction process. Second, throughout the entire oxidation process, the charge compensation in the PPy-DS film is achieved by the insertion of anions. Additionally, during the reduction process, hydrated cations are incorporated to compensate for the fixed charges associated with the anionic surfactants that form part of the mesostructure.

Although in the previous example PPy was electrochemically synthesized in the presence of the surfactant, it is worth mentioning that similar effects were observed in samples prepared via oxidative chemical polymerization.[154] In these cases, the pyrrole monomer and the surfactant, acting as organic acid dopants, were dissolved in deionized water, and an ammonium persulfate solution was gradually added to the monomer/surfactant solution under vigorous magnetic stirring. Once the material was synthesized, the PPy-surfactant samples were dissolved in m-cresol, and the solutions were spin-coated onto substrates followed by thermal treatment at 70°C in a vacuum oven.[155]

When discussing polymeric assemblies with high conductivity, it is essential to consider the use of PEDOT (poly(3,4-ethylenedioxythiophene)) as a key component in their assembly,[156,157] particularly for systems that incorporate surfactants through a layer-by-layer (LbL) assembly process. PEDOT is typically processed as a complex with PSS, where PEDOT is doped with the anionic polyelectrolyte, enhancing its functionality and facilitating integration into various applications.[158] In this context, Diforti et al.[159] have investigated surfactant-polyelectrolyte complex formation involving PEDOT using an LbL strategy, allowing for the construction of conductive channels in organic electrochemical transistors (OECTs, **Fig. 19**). These researchers demonstrated that this supramolecular strategy enables organic devices to acquire specific characteristics, adjusting the electronic properties of transistors through the controlled assembly of the anionic macromolecular complex in the presence of the surfactant cetyltrimethylammonium bromide (CTAB). The inclusion of the cationic surfactant CTAB within the LbL (**Fig. 19b**) structure induces structural modifications with significant implications for the electronic conductivity of the films. This effect is remarkable when compared to similar films assembled with the cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC). Utilizing CTAB to complex with the anionic PEDOT component resulted in a four-order-of-magnitude increase in conductance compared to integration with PDADMAC (**Fig. 19c**). This enhancement can be attributed to CTAB's positive effect on charge transport within the PEDOT matrix, likely due to the organization of conductive domains at the mesoscale. OECTs made of PEDOT:PSS/CTAB (**Fig. 19d**) demonstrated a transconductance (g_m) of 2.21 mS, and switching times of 24.2 ms for turning on and 12.3 ms for turning off the transistor. Their performance is on par with or exceeds that of PEDOT-based OECTs fabricated through more complex methods without the integration of ionic surfactants.[160,161] Additionally, the facile application of these straightforwardly produced OECTs is highlighted in the detection of the neurotransmitter dopamine, achieving a remarkable sensitivity of 279 mV/decade, a broad operational range (1−300 μM), and reliable reversibility.

6.3. Electroactive polyelectrolyte-surfactant assemblies with built-in osmium complexes

In the field of electroactive materials, one of the primary challenges is to identify systems capable of transferring electrons efficiently, rapidly, and stably. This capability is critical for the development of devices such as sensors, batteries, and fuel cells, among others. A promising approach to address this challenge lies in the use of transition metal complexes, such as osmium. Although the synthesis of such redox-active molecules can be laborious, osmium complexes as redox centers offer characteristics that are particularly attractive for the design of supramolecular electroactive materials.[162-164] The most prominent features include: (a) redox stability - osmium complexes exhibit stable oxidation states (primarily Os(II) and Os(III)), allowing for great versatility in electrochemical applications; (b) high electrochemical stability - osmium tends to be more stable compared to other transition metals, thus extending the operational life of electroactive materials based on it; (c) rapid electron transfer - osmium complexes generally facilitate fast electron transfer, which enhances the sensitivity and response speed in biosensors and electrochemical devices; and (d) redox tunability - the ligands surrounding the osmium can be easily modified to fine-tune the redox properties and optimize the electrochemical behavior, providing significant flexibility in material design.[165]

In this context, following the development by various research groups on the use of polyelectrolyte-surfactant complexes with redox activity as a strategy to construct soft electroactive materials, Cortez et al.[166] explored the complexation of polyallylamine partially bearing polypyridyl osmium complex (OsPA) with sodium dodecyl sulfate (SDS) to obtain a mesostructured, electroactive self-assembled material. The combination of these two building blocks in an aqueous medium leads to a precipitate that is soluble in dimethylformamide (DMF). Solutions of the OsPA-DS complex can be utilized to generate mesostructured films via the drop-casting technique (**Figure 20A**). X-ray reflectivity (XRR) analysis of OsPA-DS and PA-DS films, the latter used as a reference material, prepared on Si(100) substrates, revealed the presence of a third-order Bragg peak indicating lamellar organization in the characterized films.[167] Analysis of the XRR data determined that the lamellar spacing (*d*) for the PA-DS and OsPA-DS systems was 3.96 nm and 4.15 nm, respectively (**Figure 20B)**. As discussed in previous sections, the lamellar structure described by these observations is that of a microphase-separated material consisting of an ionic phase and a non-ionic phase. The ionic phase corresponds to hydrophilic domains where the polyelectrolyte chains and the ionic head groups of the surfactants coexist. Conversely, the non-ionic phase is represented by hydrophobic domains where the hydrocarbon tails of the surfactants reside.

Characterization of these films using GISAXS allows for the elucidation of the orientation of the lamellar domains with respect to the substrate (**Figure 20C)** In the case of supramolecular films of non-electroactive PA-DS, the lamellar structures are predominantly oriented parallel to the substrate. However, when a similar analysis is performed on OsPA-DS samples, it is observed that a fraction of the lamellae is oriented perpendicular to the substrate. By comparing the results obtained with the reference material, PA-DS, it can be concluded that the presence of osmium complexes within the polyelectrolyte phase induces changes in the orientation of the mesostructure. This structural reorganization likely has an impact on the electroactive properties of the film as well as its charge/mass transport characteristics, suggesting potential enhancements in performance driven by the osmium-based modifications.

Figure 21 shows the voltammogram of a 150 nm OsPA-DS film, exhibiting quasi-reversible behavior with a peak potential separation of 21 mV and a full width at half maximum (FWHM) of 110 mV, slightly larger than the value expected for an ideal one-electron redox system under finite diffusion conditions (90.6 mV). These results indicate an excellent electrochemical response of the supramolecular material as well as remarkable charge transfer characteristics. Experiments performed at different ionic strengths confirmed that ions from the electrolyte solution can permeate the film during the redox process and interact with the hydrophilic domains of the electrolyte. This behavior is a strong indicator of the outstanding properties of films obtained through this supramolecular approach, as they achieve high structural stability while maintaining efficient charge transfer capabilities.

6.4. Choosing the Optimal Redox Unit: A Comparative Analysis of Performance, Versatility, Stability, and Synthetic Complexity

Ferrocene, viologen, polyaniline, and osmium complexes are key redox-active units, each presenting distinct advantages in terms of performance, versatility, and stability across various electrochemical applications. Among these, ferrocene is particularly recognized for its well-defined and reversible redox behavior, which is driven by a single-electron transfer process (Fe^{2+}/Fe^{3+}). Its low redox potential and ease of functionalization contribute to its versatility, facilitating integration into polymers, surface coatings, and supramolecular systems.[168] However, while ferrocene remains stable in its neutral form, its oxidized state (Fe^{3+}) is prone to degradation, especially when exposed to moisture and oxygen. This limitation constrains its use in long-term or open-environment applications unless it is protected within a stable matrix or hydrophobic environment. Consequently, ferrocene is best suited for applications that require short-term redox cycling or where its oxidized form can be quickly reduced. The synthesis of ferrocene is relatively straightforward, typically involving metal-organic reactions, although functionalization can introduce additional complexity.

In contrast, viologens undergo efficient two-electron redox transitions, which make them particularly well-suited for applications such as electrochromic devices, molecular switches, and redox flow batteries. These units can cycle between their dicationic, radical cationic, and neutral forms.[169] While viologens demonstrate versatility in aqueous solutions, their radical cations are sensitive to oxygen, leading to potential instability and degradation over time. Nonetheless, in controlled environments or encapsulated systems, viologens exhibit reliable performance, making them effective in electrochemical applications that require multiple redox states. Their synthesis is achieved through Menshutkin reactions between 4,4'-bipyridine and alkyl halides, with the creation of derivatives potentially increasing synthetic complexity.

Similarly, polyaniline (PANI) is a conductive polymer renowned for its ability to switch between various oxidation states, thereby enhancing its versatility in sensors, supercapacitors, and energy storage devices. The polymerization of aniline requires controlled conditions - such as the careful selection of oxidants and solvents - to achieve the desired molecular weight and properties. The redox behavior of PANI can be tuned by adjusting pH and doping levels, providing flexibility for diverse electrochemical systems. Its conductivity and redox properties are particularly effective in neutral and mildly acidic environments; however, stability may degrade under extreme pH conditions. Despite this, its capability to transition between conductive and non-conductive states grants PANI a high degree of adaptability across a wide range of applications.

Osmium complexes, on the other hand, are distinguished by their rapid and reversible redox kinetics, alongside a broad range of redox potentials that can be finely tuned through ligand modifications. These properties make them especially useful in bioelectrochemical systems and electrocatalysis, where their multi-electron transfer capability enhances overall efficiency. Notably, osmium complexes exhibit high stability in biological and aqueous environments, positioning them as ideal candidates for biosensors[170] and biocatalytic systems. While they may show sensitivity to extreme pH or oxidative conditions over time, their overall stability and ability to effectively interact with biomolecules provide significant advantages in bioelectronic applications. However, it is important to note that this type of compound can only be scaled for clinical or fine chemical applications due to the limited availability of osmium as a raw material.

Ultimately, the selection of a redox unit demands careful consideration of the specific characteristics desired, as well as a thorough evaluation of the requirements of the system. It is crucial to weigh these factors against the advantages and disadvantages inherent to each molecular system. It is important to note that, in the previously discussed examples, the focus of the analysis is primarily on redox activity rather than electroactivity. Historically, the terms electroactive and redox-active have often been used interchangeably, but they have distinct meanings in electrochemistry and materials science. Electroactive materials respond to electrical stimuli but may or may not undergo redox reactions. In contrast, redox-active materials must undergo oxidation-reduction processes as part of their function.

7. Redox-active self-assembled polyelectrolyte–surfactant complexes integrating enzymes on electrodes.

The successful integration of enzymes into or onto electroactive ionic self-assembly (ISA) systems has marked a significant breakthrough in the field of bioelectrochemistry. Enzymes, as biocatalysts, provide exceptional specificity and efficiency for biochemical reactions, and their incorporation into electroactive ISA materials holds transformative potential for the development of electrochemical sensors, bioelectrodes, and biosensors. From a preparative chemistry standpoint, ISA offers a distinctive method for enzyme immobilization by enabling the creation of nanostructured supports with tailored surface properties. Through ISA, it is possible to generate films with tailored surface characteristics that enhance enzyme binding and catalytic activity.

By combining the ability of ISA to precisely control the assembly of enzymes - ensuring their uniform distribution and optimal loading on various substrates - with its capacity to incorporate redox centers that facilitate efficient electron transfer, it has become feasible to design highly versatile platforms for the development of electrochemical biosensors with enhanced sensitivity and specificity.

A noteworthy aspect of the assembly of polyelectrolyte–surfactant complexes is the ability to use aqueous media during the processing of samples. This feature is particularly significant when working with enzymes, as their intrinsic bioactivity can be severely compromised in the presence of non-aqueous solvents. The use of aqueous environments not only preserves the functional integrity of enzymes but also offers a more biocompatible platform for developing enzyme-based electroactive systems. In this context, Cortez *et al.*[171] proposed a simple yet effective method for the incorporation of enzymes into redox-active ISA films. This method follows a two-step procedure, where an aqueous suspension of the polyelectrolyte–surfactant complex is first applied onto a substrate via casting. Subsequently, the enzyme glucose oxidase (GOx) is assembled onto the film by exposing it to an enzyme solution, forming the OsPA–DS_{aq}/GOx system (**Figure 22**).

This approach preserves the inherent capabilities of ionic self-assembly (ISA), which combines polyelectrolytes and surfactants, in an environment compatible with the natural activity of the enzyme.

As mentioned previously, the nature of the solvent significantly affects the properties of the resulting ISA films. To elucidate these effects, we can compare the structural characteristics of films prepared from aqueous solutions versus those prepared in dimethylformamide (DMF). A detailed analysis using GISAXS reveals that both films, when in a "dry" state, exhibit a lamellar structure (**Figure 23**). However, upon exposure to a high-humidity environment, a notable difference arises: the film formed in DMF (OsPA–DSorg) retains its mesostructure, while the film obtained from the aqueous processing condition (OsPA–DSaq) transitions to an amorphous structure. Remarkably, this structural change does not compromise the stability of the film when immersed in aqueous solutions. This stability is further corroborated by the voltammetric characteristics of the films (**Figure 24**), in which OsPA–DSaq/GOx demonstrates greater sensitivity to glucose compared to the response observed with the OsPA–DSorg/GOx systems.

This difference in sensitivity has been attributed to the increased hydrophilicity and amorphous nature of the OsPA–DSaq films, which facilitate interactions between GOx and the redox centers hosted within the film, as well as enhance the diffusion of glucose molecules within the interfacial architecture.

8. Ionic self-assembly of electroactive biorecognizable units

The integration of biorecognition sites into ionic self-assembly (ISA) films represents a significant innovation that boosts the functionality and performance of these materials across various (bio)electrochemical applications.[172] One of the most notable aspects of this integration is the specificity and selectivity it offers. Biorecognition sites enable films to selectively recognize and bind to target molecules, such as biomolecules, resulting in more precise and efficient assembly and integration processes. This capability is particularly valuable in the preparation of biosensors and other electrochemical devices.[173-175] Furthermore, this approach contributes to improved stability and functionality of the enzymes and biomolecules embedded within the films, safeguarding them against denaturation or degradation, thus translating into more durable and reliable performance. Additionally, these films can be easily integrated with other technologies, such as microfluidic systems, broadening their application potential in clinical diagnostics and biomedical monitoring.

The customization and adaptability of biorecognition sites also serve as a key advantage. Their chemistry can be modified to suit different applications, allowing for the tailored design of ISA films according to specific needs. For these reasons, incorporating biorecognition sites into ISA films not only optimizes device functionality but also opens up new possibilities for their application in various technological fields. As previously mentioned, the immobilization of enzymes onto ISA films is critically important for constructing biosensors. Among the wide variety of enzymes applicable in bioelectrochemistry, glycoenzymes, such as glucose oxidase and horseradish peroxidase (HRP), hold a prominent place due to their utility in a diverse range of transduction processes and amplification of bioelectrochemical sensing activities.

It is well-known that glycoenzymes can be immobilized onto surfaces through the use of lectins, biomolecules capable of recognizing the glycosylated portions of glycoenzymes.[176] Within this paradigm, the combination of ISA with biorecognition-mediated assembly has made notable contributions to the development of supramolecular materials compatible with the preparation of modified electrodes suitable for use in electrochemical biosensors. Cortez et al. implemented the use of a multifunctional polyelectrolyte capable of forming mesostructured polyelectrolyte-surfactant complexes via ionic interactions, exposing ligands capable of participating in biorecognition-driven assembly processes of glycoproteins, and facilitating electron transfer between the redox center of the enzyme and the electrode surface, often referred to as “redox wiring.” [177,178]

This multifunctional polyelectrolyte features a polyallylamine backbone onto which osmium bipyridyl complexes (redox units) and lactose moieties (biorecognizable units) are grafted **(Figure 25**). This polyelectrolyte is water-soluble and, in the presence of sodium dodecyl sulfate (SDS), forms a precipitate that is easily redispersible in dimethyl sulfoxide (DMSO) (GOsPA-DS). Through simple processes such as spin-coating or drop-casting, these solutions facilitate the preparation of stable mesostructured films with excellent adhesion to modified electrode surfaces. GISAXS characterization corroborated that these films exhibit predominantly parallel lamellar organization with a smaller fraction displaying multi-orientation. Furthermore, the electrochemical characterization of these films revealed a quasi-reversible electrochemical process, indicating rapid intrafilm electron transfer.

As described in **Figure 25,** the multifunctional polyelectrolyte contains functional groups that can be biorecognized by lectins, such as concanavalin A (Con A). This strategy, wherein the assembly process is mediated by Con A, significantly enhances the immobilization of the glycoprotein horseradish peroxidase (HRP) with a high degree of efficiency. HRP is an enzyme that, due to its intrinsic properties, is often challenging to anchor onto surfaces using non-covalent strategies. In this case, the use of the lectin notably contributes to the formation of HRP monolayers on the electrode surface effectively, without altering or denaturing the enzyme. Furthermore, since Con A can act as an insulating element in the interfacial architecture, the researchers who proposed this method employed Con A labeled with redox-active osmium complexes to mediate the electrical communication between HRP and the electrode through the multifunctional ISA film.

9. Redox-Active Self-Assembled Nanoparticle−Polyelectrolyte−Surfactant Composite Thin Films

It is well established that in the case of amperometric electrochemical biosensors, the sensitivity of these devices is significantly influenced by various factors, including substrate diffusion near the electrode, the chemical nature of the redox mediators, and the electrical connectivity between the recognition elements and other transduction components operating within the device. Take, for instance, an enzymatic glucose biosensor: the electrical communication between glucose oxidase and the transducer (composed of the mediator/electrode system) is the predominant factor determining the overall performance of the electrochemical device. The incorporation of nanoparticles into modified electrodes for use in enzymatic biosensors has proven to be an extremely effective strategy as nanoparticles can be readily integrated on the electrode surface and facilitate electron transfer between the enzyme and the electrode.[179] Specifically, gold nanoparticles exhibit high electrical conductivity, optimizing the connection between the active sites of biomolecules, redox centers within the film, and the electrode surface, thereby enhancing the electrochemical response.[180]

In recent decades, this approach has gained considerable relevance, prompting the integration of metallic nanoparticles to be explored in various contexts aimed at improving electron transfer between the enzyme and the electrode.[181,182] As an alternative strategy, the use of ionic self-assembly (ISA) based on polyelectrolyte-surfactant complexes offers similar functional versatility, while also providing the advantage of being a straightforward and direct experimental method for electrode modification. A series of studies focused on the functionalization of metal electrodes with gold nanoparticles embedded in films of OsPA-DS polyelectrolyte-surfactant complexes have demonstrated significant improvements in the electron transfer properties of the redox centers hosted within the film, as well as a notable enhancement of the catalytic behavior of glucose oxidase (GOx).[183]

These hybrid systems were prepared by mixing a suspension of Au NPs with a solution of the OsPA-DS complex in DMF, where the resulting suspension was used to modify the electrode surface via spin coating **(Figure 26**). The integration of the nanoparticles into the film had a remarkable effect on the electrochemical connectivity of the redox centers. For films prepared in the absence of nanoparticles, the fraction of redox centers "wired" to the metallic electrode was approximately 64%, whereas this percentage reached 100% in identical films containing nanoparticles.

When the OsPA-DS-AuNP films were characterized by GISAXS, they were found to lack lamellar organization and were not mesostructured **(Figure 27**). This experimental evidence clearly indicates that while the integration of metallic nanoparticles significantly enhances the electroactivity of the films, it also substantially disrupts its mesoscale organization.

The electrochemical characterization of both systems reveals that the bioelectrocatalytic current densities obtained from electrodes incorporating Au NPs within the film exceed by more than double the current values observed in films without Au NPs. This remarkable difference can be corroborated by the data in **Figure 28,** where it is evident that the catalytic currents in response to increasing glucose concentrations are significantly higher in the case of OsPA-DS-AuNP films. Quantitatively, the sensitivity of OsPA-DS-AuNP films to glucose is five times greater than that of OsPA-DS films within the physiological concentration range. These results illustrate the profound effect that AuNPs exert on the communication between glucose oxidase (GOx) and osmium centers, acting as facilitators of the electron transfer process.

It is worth noting that the solvent used in the processing of ISA films has a pronounced influence on both the meso-organization and bioelectrochemical properties of the composite film.[184] It has been found that the solvent used in the fabrication of ISA films containing Au NPs notably affects not only the morphological and meso-organizational characteristics of the film but also the efficiency and performance of the resulting bioelectrochemical system.

For electrodes supramolecularly modified with OsPA-DS-AuNP/GOx films, two distinctive electrochemical features are attributed to the solvent and the presence of nanoparticles, respectively. Electrodes modified using aqueous processing (**Figure 29)** exhibit higher sensitivity to glucose at low glucose concentrations, with the signal saturating at 25 mM glucose. In contrast, the bioelectrocatalytic signal from electrodes processed with organic solvents reaches its maximum at 50 mM glucose (**Figure 30**). This implies that bioelectrodes cast from aqueous solutions are more sensitive to glucose under low-concentration conditions. The higher glucose sensitivity of the aqueous-processed electrodes has been attributed to the increased hydrophilicity of these films, which in turn facilitates the access of glucose molecules to the interfacial architecture. Additionally, the presence of Au NPs enhances the catalytic response of the films regardless of the solvent used, although this effect is more prominent when organic solvents are employed.

10. Meso-Organized (Bio)Functional Electrodes via Layer-by-Layer Assembly of Enzymes, Redox Polyelectrolytes, and Surfactants

In a previous section, we have discussed that it is possible to construct films of polyelectrolyte-surfactant complexes with a high degree of organization using a layer-by-layer (LbL) assembly technique. This same approach is equally valid for generating ionic self-assembled (ISA) films that incorporate enzymes within their mesostructure. It has been shown that utilizing lipid-like surfactants allows for the synthesis of stacked multilayers integrating glucose oxidase (GOx) and polyallylamine bearing redox-active units into the stratified hydrophilic domains of a phase-segregated architecture through layer-by-layer assembly.

One of the predominant areas in nanoarchitectonics is the development of strategies that facilitate the assembly of molecular building blocks onto solid surfaces in predetermined arrangements for the fabrication of functional three-dimensional assemblies. In this regard, Cortez and co-workers[185] have demonstrated the fabrication of stratified multilayer films through the sequential layer-by-layer assembly of a redox-active osmium complex tagged poly(allylamine) hydrochloride (OsPA), sodium dodecylphosphate (DP), and glucose oxidase (GOx), resulting in the formation of multicomposite molecular assemblies, specifically OsPA/DP/OsPA/GOx multilayers (**Figure 31**).

Characterization of these films using grazing incidence small-angle X-ray scattering (GISAXS) clearly indicates the presence of meso-organization, interpreted as the formation of lamellar domains predominantly oriented parallel to the substrate, with a minor fraction oriented randomly (**Fig. 32a**). When this same structure was tested in a high-humidity environment, an increase in the lamellar spacing from 3.0 to 3.4 nm was observed due to the presence of water in the hydrophilic domains (**Fig. 32b**). These results are particularly noteworthy as they demonstrate that the meso-organization (*i.e.,* stratification) of the film is not adversely affected by the presence of water. It is presumed that the strong electrostatic and ion-pairing interactions between the amino groups of polyallylamine hydrochloride (PAH) and the phosphate groups of DP, along with the hydrophobic forces introduced by the alkyl chains, are responsible for the formation of a highly organized and morphologically stable structure in the presence of an aqueous medium. One way to understand this is to view the lipid-like surfactant bilayers as barriers that inhibit the interdiffusion of the polyelectrolyte chains confined within the interfacial architecture, thereby imparting dimensional stability to the nanoarchitected film.

Figure 32d illustrates the voltammetric responses of gold electrodes modified with $(OsPA/DP/OsPA/GOx)_5$ multilayers in both the absence and presence of glucose. In the absence of glucose, the observed electrochemical signal is attributed exclusively to the reversible redox response of the osmium centers. Upon exposure of the assembly to 50 mM glucose, a marked increase in the oxidation current is observed, along with a decrease in the reduction current. This behavior is associated with the redox mediation of the GOx-catalyzed oxidation of glucose. The electrochemical behavior demonstrated in the figure illustrates the responsiveness of the film to the presence of glucose in the electrolyte solution. Note that by adding OsPA as a capping layer over a layer-by-layer (LbL) assembly significantly enhances the biosensor response (**Fig. 32e**). This effect has been attributed to the fact that this capping layer improves the electron transfer efficiency of the whole assembly. This LbL strategy constitutes a rapid and experimentally simple method for creating complex stratified multilayers with precise control over layer composition and thickness. The versatility of this approach may be particularly beneficial in cases where there is a desire to construct films with spatial segregation of individual components in nanocompartmentalized stratified domains.

Summary and Outlook

The ionic self-assembly (ISA) of polyelectrolyte-surfactant systems exemplifies a powerful nanoarchitectonic approach for designing hierarchical soft materials with tailored electrochemical and biofunctional properties. By harnessing the rich interplay between electrostatic and hydrophobic interactions, these systems enable precise molecular organization, facilitating the construction of mesostructured architectures with redox-active, and adaptive functionalities. The inherent modularity of polyelectrolyte-surfactant complexes positions them as versatile building blocks for nanoarchitectonic strategies aimed at creating advanced bioelectrochemical platforms, including biosensors, and diagnostic interfaces.

Looking ahead, the challenge lies in further expanding the applicability of these systems to address the growing demands for multifunctional bioelectrochemical interfaces. Polyelectrolyte-surfactant complexes possess inherent advantages, such as their capacity for dynamic self-organization and responsiveness to external stimuli, making them ideal candidates for constructing adaptive bioelectrochemical platforms. For instance, their ability to immobilize biorecognition elements, such as enzymes, within highly ordered and electroactive matrices can significantly enhance the sensitivity and selectivity of biosensors. Furthermore, the exploration of redox-active systems derived from tailored polyelectrolytes offers promising opportunities for developing soft materials optimized for energy storage and conversion.

Future efforts should focus on advancing the design rules governing these assemblies to achieve greater control over hierarchical organization and interfacial properties, particularly in the context of bioelectrochemical systems. Combining ISA with complementary methodologies – such as block copolymer self-assembly, molecular frustration, or hybrid organic-inorganic approaches – can enable the creation of complex, multi-length-scale architectures tailored for specific bio(electro)functional applications. Additionally, integrating ISA processes with cutting-edge analytical techniques and machine learning tools will not only enhance the understanding of self-assembly dynamics but also accelerate the development of optimized materials for real-world applications.

Ultimately, the versatility of polyelectrolyte-surfactant complexes within the ISA framework positions them as key players in the advancement of functional materials for bioelectrochemical systems. By drawing inspiration from biological processes and embracing interdisciplinary approaches, researchers can unlock the full potential of these materials, paving the way for innovative solutions in health diagnostics, energy systems, and beyond. The path from molecular assembly to functional bioelectrochemical devices is filled with challenges, but the opportunities to redefine the landscape of bioelectrochemical nanoarchitectonics are immense and inspiring.

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Statement of Novelty

This work explores ionic self-assembly as a nanoarchitectonic strategy for designing hierarchical materials with tunable electrochemical properties, emphasizing their potential for bioelectrochemical interfaces and future integration with complementary self-assembly approaches.

Biographies

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Lorena Cortez obtained her degree in Biochemistry from the Universidad de Buenos Aires (FFyB - UBA), Argentina, in 2006. She completed her PhD in Chemistry at UBA (FCEN – INQUIMAE - UBA) in 2011. She conducted postdoctoral research at the Soft Matter Laboratory (INIFTA). She is a research staff member of CONICET at INIFTA. Her research focuses on the design of functional macromolecular nanoarchitectures, including the development of nanoparticles and surfaces with tailored functional properties for the controlled release of bioactive molecules, as well as the design of supramolecular materials and surface modification techniques for the fabrication and optimization of biosensors.

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Dr. Esteban Piccinini is a Tenured Scientific Researcher at the National University of La Plata (UNLP, Argentina) and the Scientific Leader of Gisens Biotech Corporation (USA). He earned his BS in Chemistry in 2014 and his PhD in Chemistry in 2019, both from UNLP. He completed a research specialization in 2D semiconductor materials at the Austrian Institute of Technology (in Vienna). He was awarded the Leloir Prize (UBA) for the best doctoral thesis in chemistry. In 2022, he received the recognition Innovator Under 35 by *MIT Technology Review*. His research focuses on Organic Bioelectronics.

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After receiving a B.S. in Chemistry from the National University of La Plata (2003), he completed a Ph.D. on simulations and experiments in heterogeneous catalysis under vacuum, supervised by Prof. Vicente (UNLP) and Prof. Imbihl (University of Hannover). During postdoctoral research, he focused on the synthesis and applications of meso- and microporous materials. Since joining the Softmatter Lab in 2011, and following a research stay in Prof. Matzger's lab at the University of Michigan, his work has centered on Microporous Coordination Polymers (MOFs). Current projects explore MOF-based composites - both in colloidal and film form - for energy and sensing applications, leveraging interdisciplinary collaboration and advanced characterization techniques.

Waldemar Marmisollé
Waldemar Marmisolle graduated in Chemistry from the Universidad Nacional de La Plata (UNLP), Argentina, in 2007 and also completed his PhD in Chemistry at UNLP in 2011. He is a research staff member of CONICET at INIFTA and a Professor of Physical Chemistry at UNLP. His research focuses on the physicochemical aspects of electrochemical processes and the construction and characterization of electroactive materials.

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He is a Full Professor at the University of Buenos Aires and a Senior Research Staff member at the Argentine National Research Council (CONICET). Throughout his career, he has established a laboratory dedicated to the development and characterization of materials, with the primary objective of their application in sensors. More recently, his work has expanded to include the development of alternative methods for power generation. His current research focuses on designing devices for detecting clinically and environmentally relevant species using functional DNA, as well as studying energy generation through systems that facilitate efficient electron transfer processes for use in biofuel cells and flow batteries.

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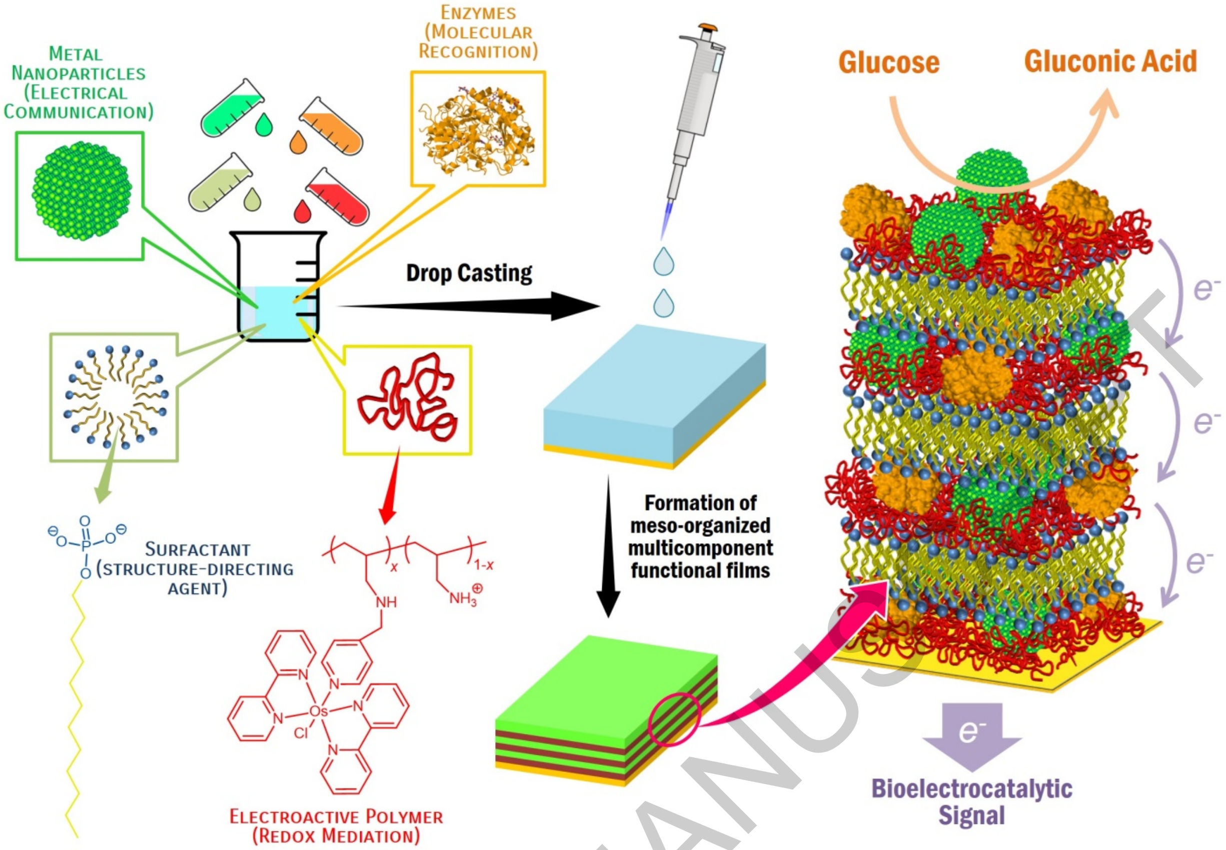
Omar Azzaroni, a chemist, earned his Ph.D. from Universidad Nacional de La Plata (Argentina) in 2004. He conducted postdoctoral research at the University of Cambridge (UK) (2004–2006) and the Max Planck Institute for Polymer Research (Germany) (2007). He led a Max Planck Partner Group from 2009 to 2013 and served as Vice-Director of INIFTA (2012-2015). Currently, he is a fellow member of CONICET, heads the Soft Matter Laboratory at INIFTA, and is a Full Professor at UNLP. His research focuses on integrating functional molecular systems into devices like solid-state nanopores, graphene-based transistors, and bioelectrochemical sensors. More details: https://softmatter.quimica.unlp.edu.ar.


Metal Nanoparticles (Electrical Communication)
Enzymes (Molecular Recognition)
Surfactant (Structure-directing agent)
Electroactive Polymer (Redox Mediation)
Drop Casting
Formation of meso-organized multicomponent functional films
Glucose
Gluconic Acid
e⁻
e⁻
e⁻
e⁻
Bioelectrocatalytic Signal

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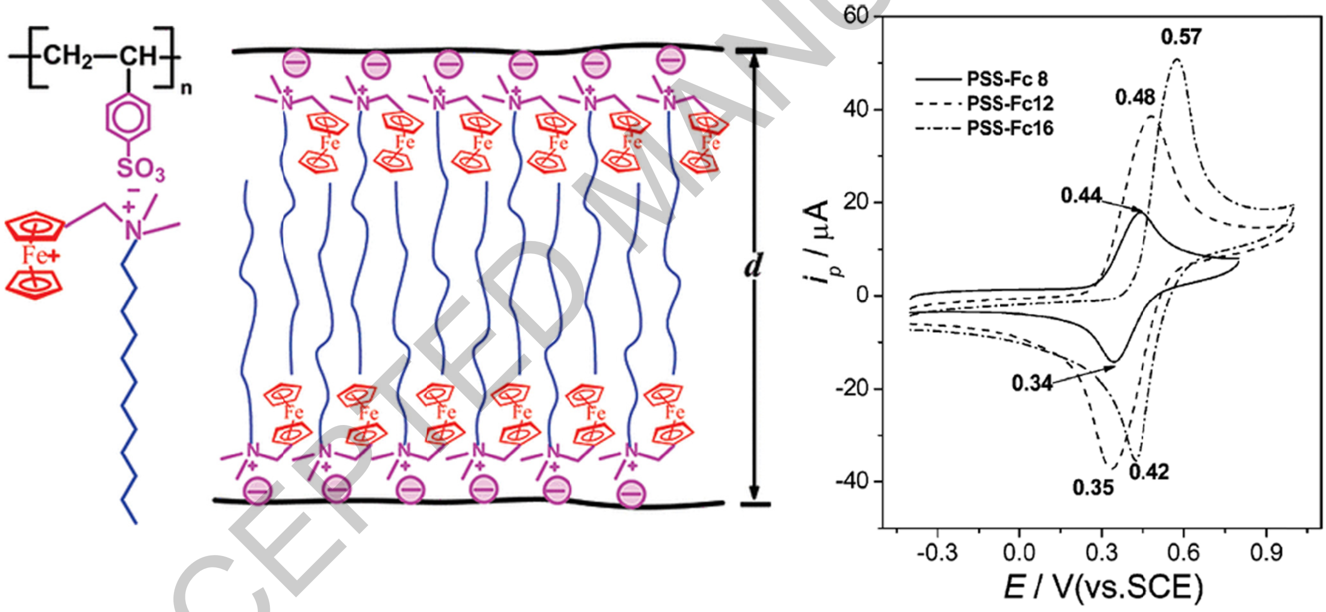

Figure 1. (Left) Schematic depiction of PSS-Fc$_n$ complex. (Right). Cyclic voltammograms of PSS-Fc8, PSS-Fc12, and PSS-Fc16 complexes measured at a scan rate of 0.2 V/s in 0.1 M NaCl solution (T = 25 °C). Reproduced from [95]. With permission from American Chemical Society.

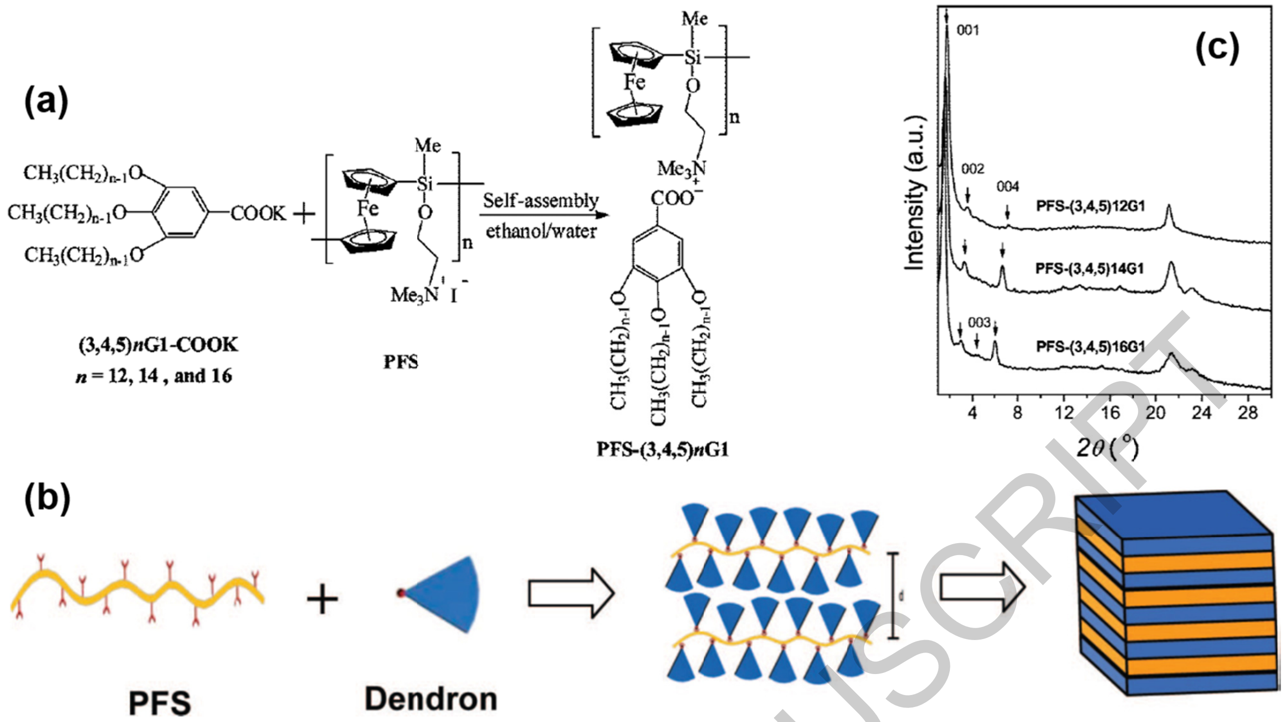

Figure 2. (a) Schematic depicition of complex preparation. (b) Stacking model for the complexes at room temperature. (c) XRD profiles of the PFS-(3,4,5)$_n$G1 (n = 12, 14, 16) complexes at room temperature. Reproduced from [97]. With permission from American Chemical Society.

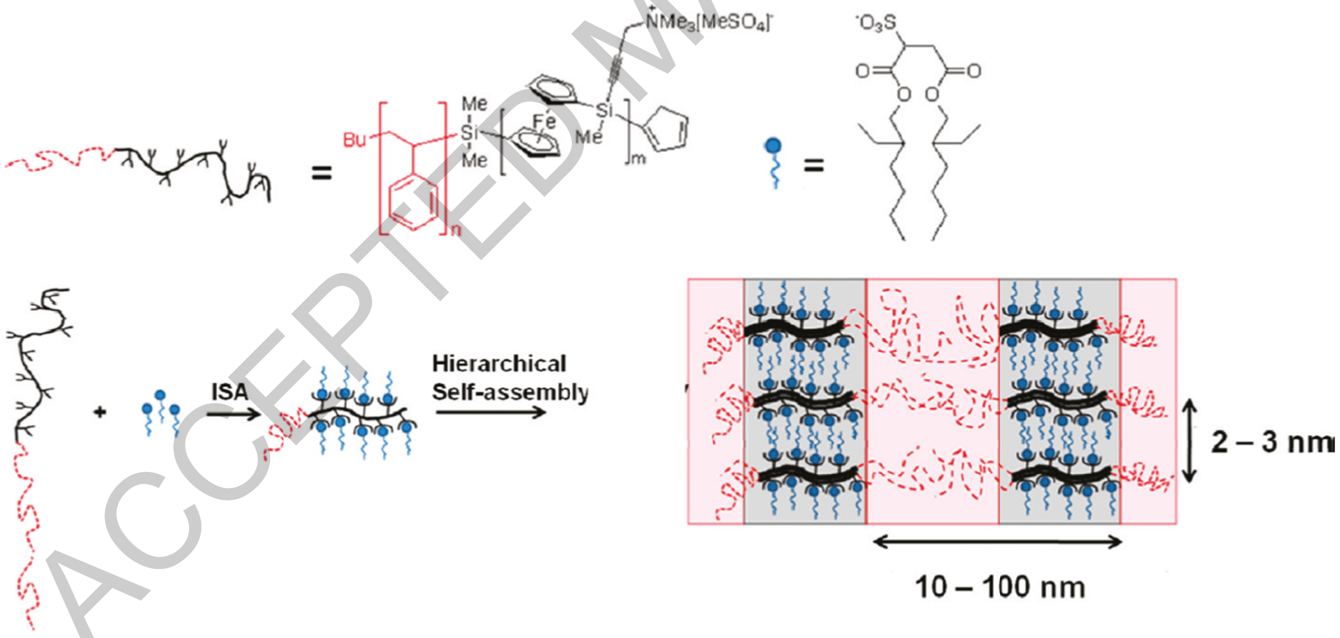

Figure 3. Schematic representation of the formation of hierarchically self-assembled architectures, illustrating the concept of structure-within-structure formation. Reproduced from [99]. With permission from American Chemical Society.

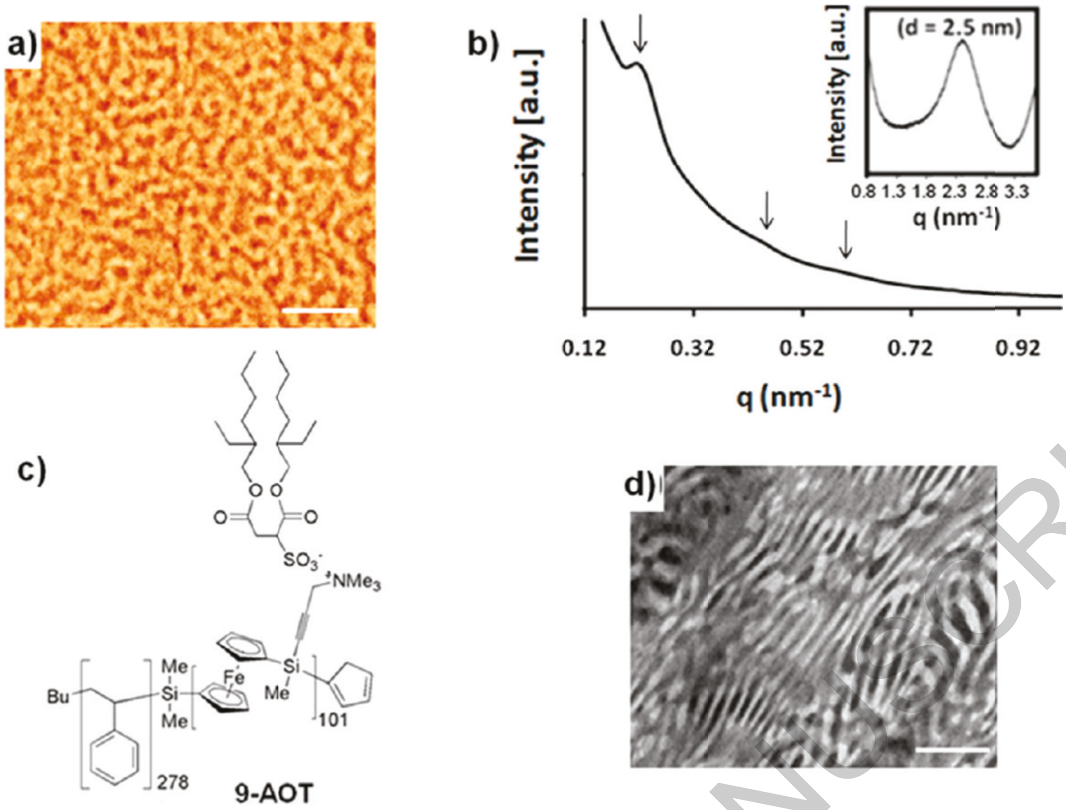

Figure 4. Morphological characterization of 9-AOT. (a) AFM phase profile, scale bar = 200 nm. (b) SAXS scattering of the sample. (c) Structure of the complex. (d) TEM micrograph of microtomed sections (60 nm), annealed for 5 days at 130 °C (scale bar = 200 nm). Reproduced from [99]. With permission from American Chemical Society.

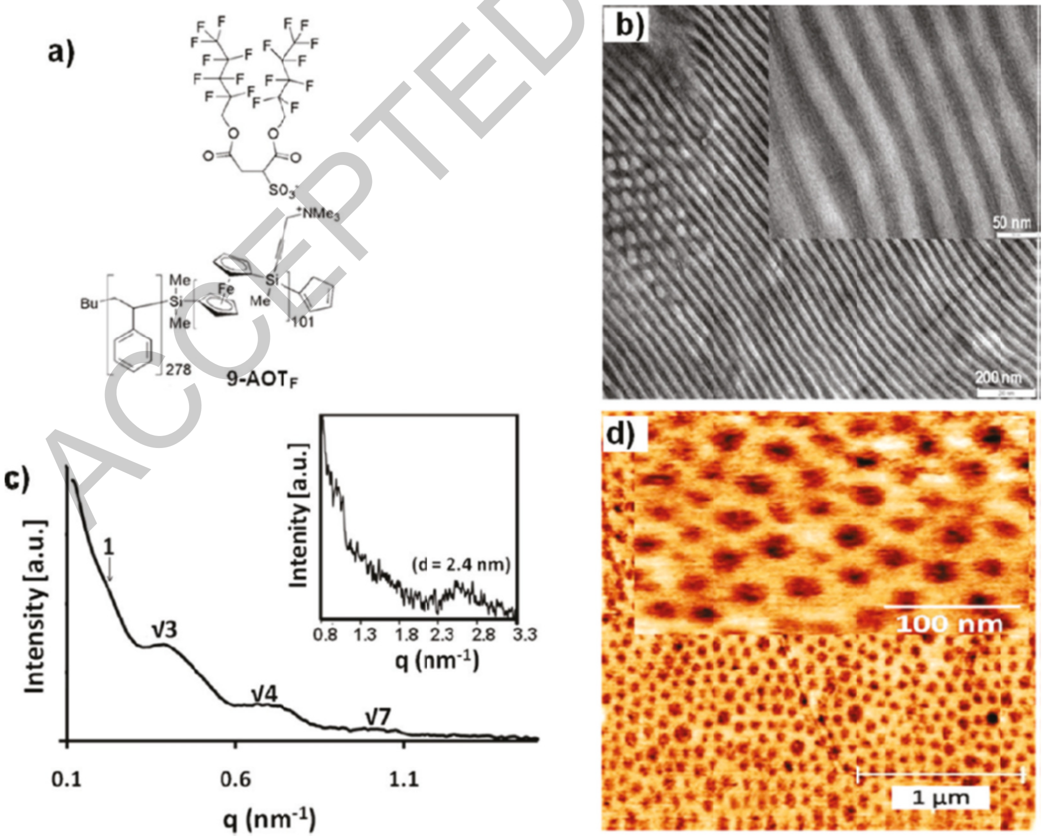

Figure 5. (a) Structure of the complex 9-AOTF. (b) TEM micrograph of microtomed sections at 60 nm. (c) SAXS patterns at small and large length scales. (d) AFM phase profile showing the cylinders after etching the organic block with an oxygen plasma. Reproduced from [99]. With permission from American Chemical Society.

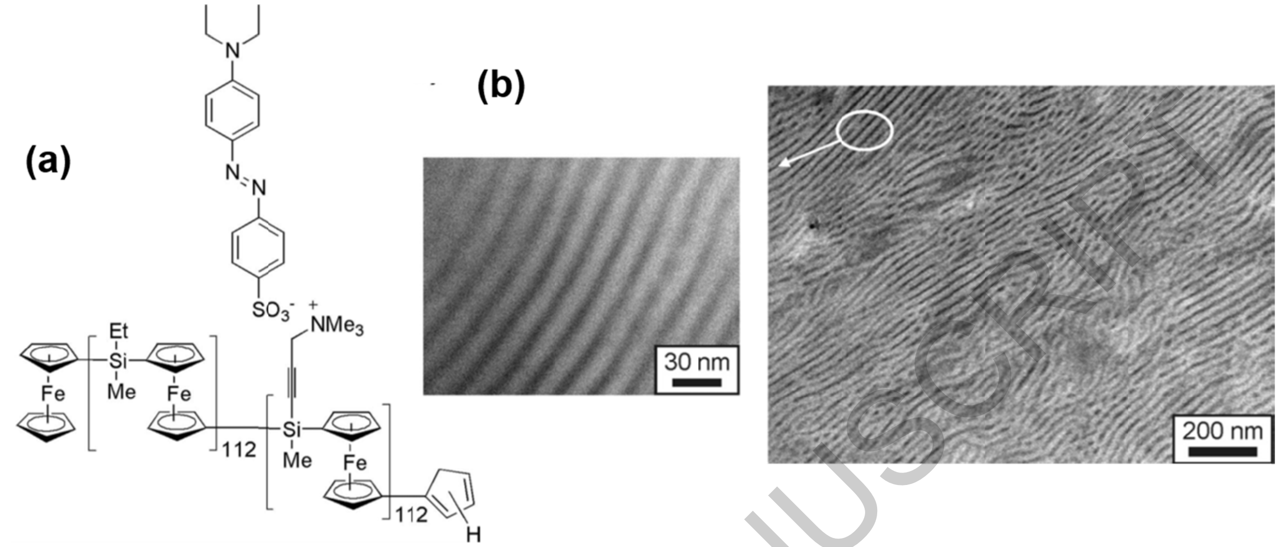

Figure 6. (a) Chemical structure of the hierarchical PFEMS$_{112}$-*b*-PFAMS(EO)$_{112}$ complex. (b) TEM micrographs of the microphase-separated PFEMS$_{112}$-*b*-PFAMS(EO)$_{112}$ complex at different magnifications. Reproduced from [101]. With permission from VCH-Wiley.

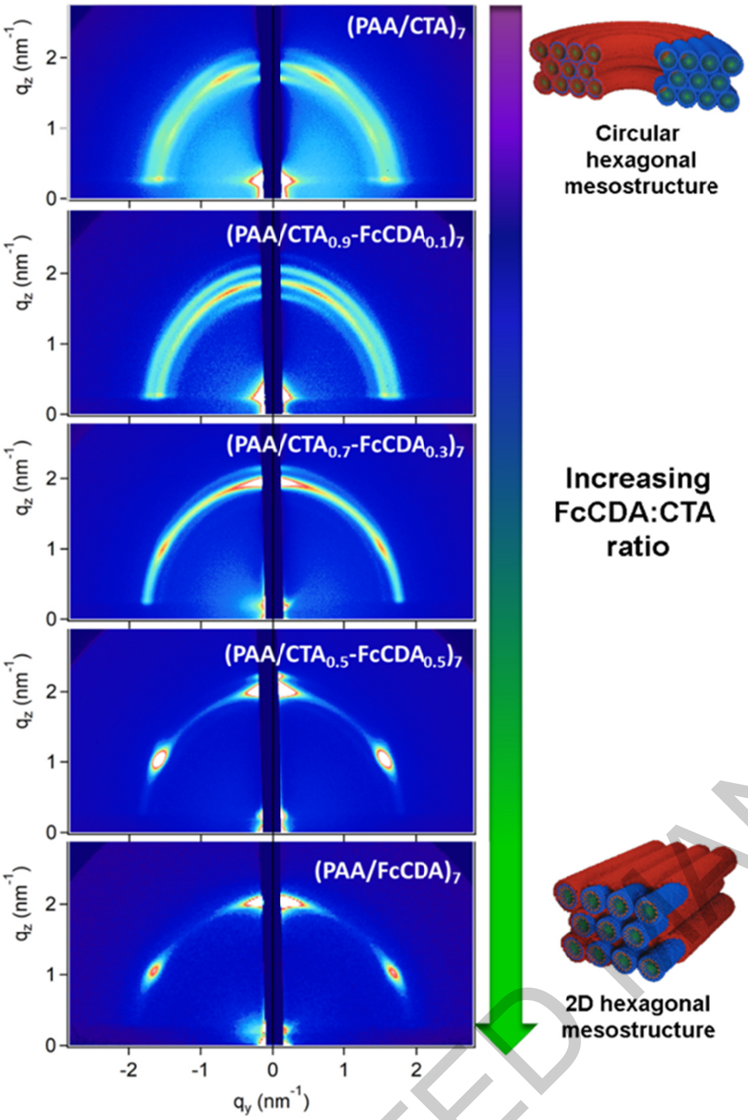

Figure 7. GISAXS patterns for (PAA/surfactant)$_7$ assemblies prepared on Si (100) substrates with different CTA:FcCDA ratios. From top to bottom, molar fraction of FcCDA in solution: 0, 0.1, 0.3, 0.5 and 1. Reproduced from [103]. With permission from VCH-Wiley.

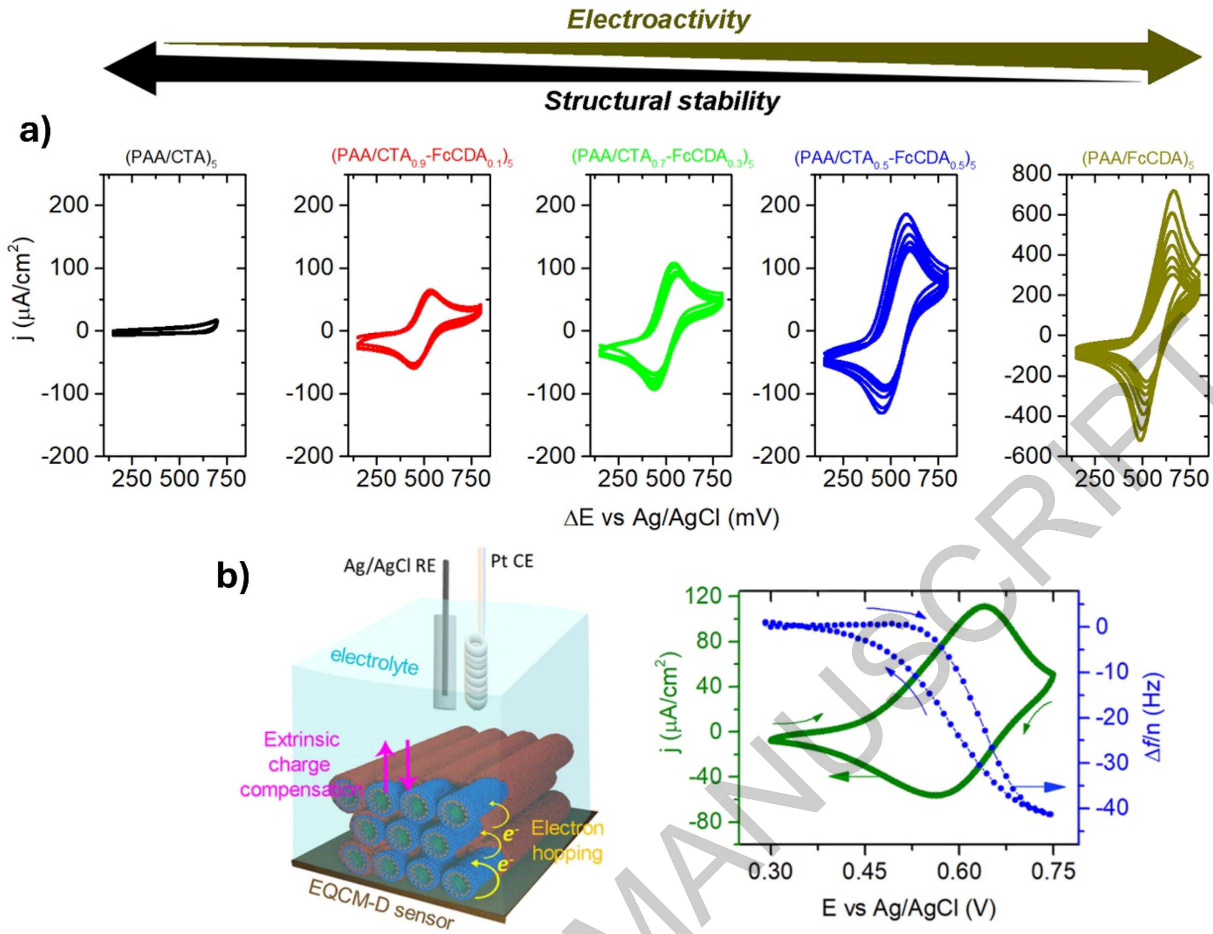

Figure 8. a) Cyclic voltammograms for assemblies (PAA/surfactants)$_5$ with different CTA:FcCDA ratios. From left to right: (PAA/CTA)$_5$, black; (PAA/CTA$_{0.9}$-FcCDA$_{0.1}$)$_5$, red; (PAA/CTA$_{0.7}$-FcCDA$_{0.3}$)$_5$, green; (PAA/CTA$_{0.5}$-FcCDA$_{0.5}$)$_5$, blue; and (PAA/FcCDA)$_5$, brown. Voltammogram cycle number: 1, 5, 10, 15, 20, 25 and 30. Scan rate: 50 mV/s. b) Left: scheme of the EQCM-D experimental setup. Right: EQCM-D response for a (PAA/CTA$_{0.5}$-FcCDA$_{0.5}$)$_7$/PAA assembly. Current density (*j*) and frequency, *Δf,* as a function of the applied potential. Supporting electrolyte:100 mM NaCl. Scan rate: 25 mV/s. Adapted from [103] and [104] with permission from Wiley-VCH Verlag GmbH & Co. and Elsevier, respectively.

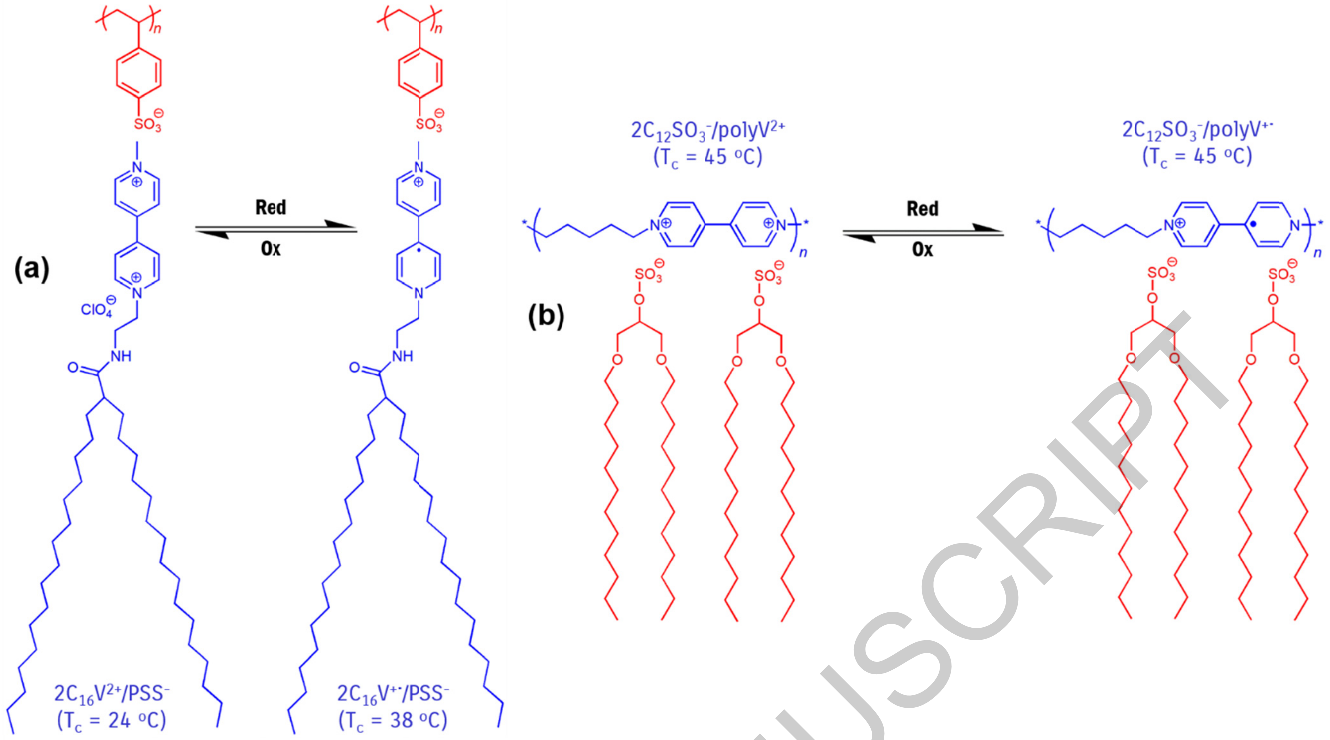

Figure 9. Chemical structure of (a) $2C_{16}V^{2+}/PSS^-$ and (b) $2C_{12}SO_3^-/polyV^{2+}$ complexes.

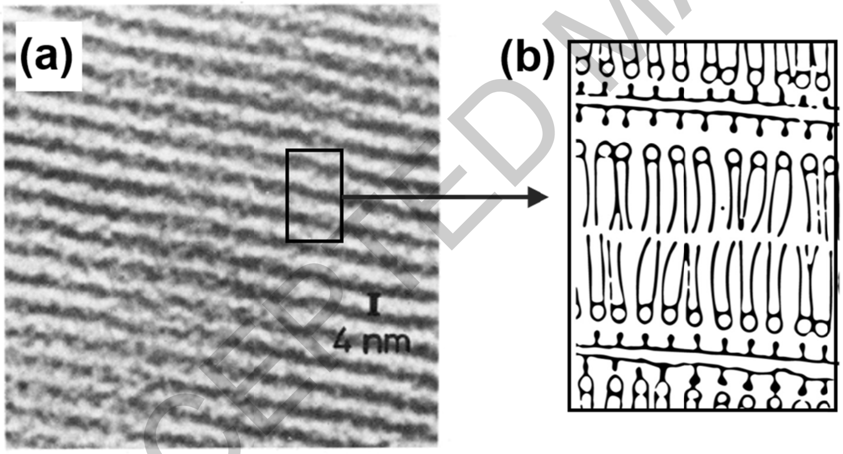

Figure 10. (a) Transmission electron micrograph and (b) and the illustration (c) of the intersection of the $2C_{16}V^{2+}$/PSS film. Reproduced from [114]. With permission from American Chemical Society.

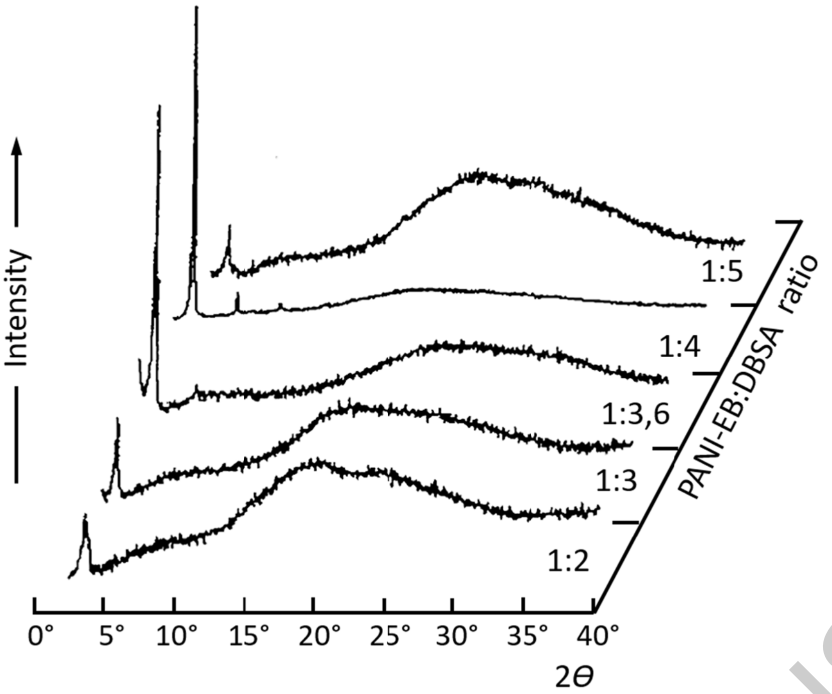

Figure 11. X-ray diffraction patterns of the complexes made from different PANi:DBSA weight ratios (doping temperature: 100°C; doping time: 20 min). Reproduced from [127]. With permission from VCH-Wiley.

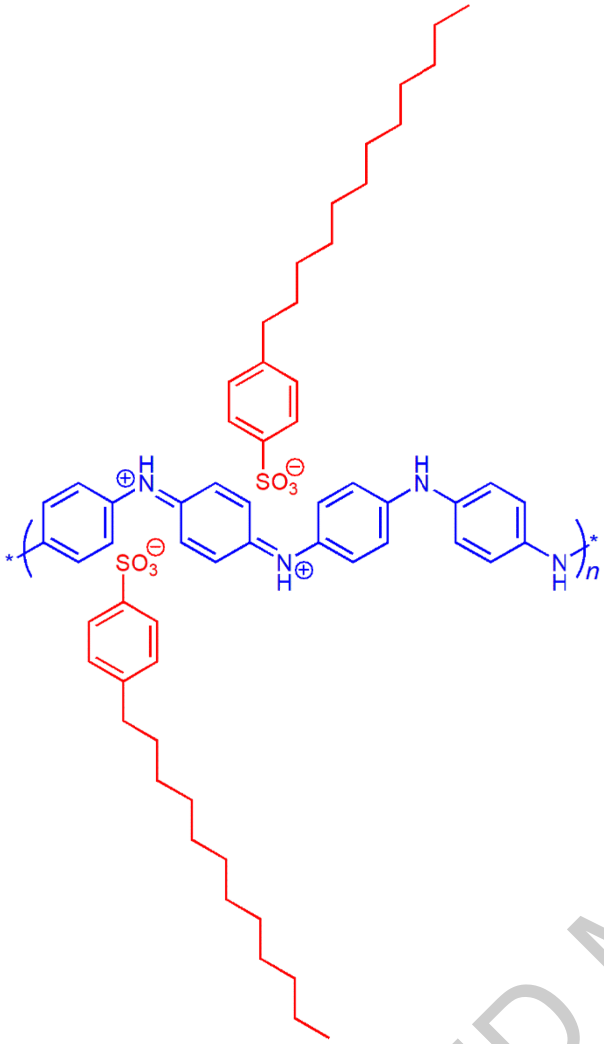

Figure 12. Chemical structure of the PANI-DBSA complex.

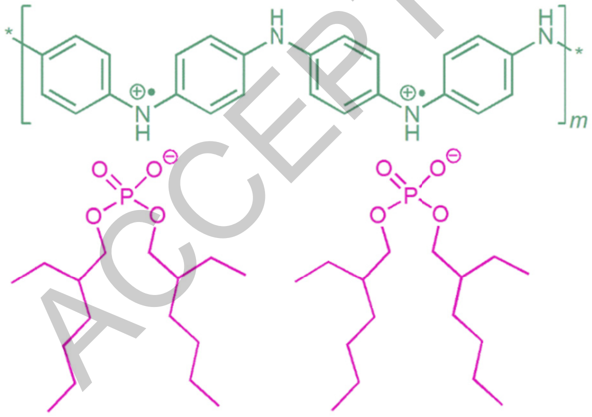

Figure 13. Chemical structure BEHP–oligomer complex.

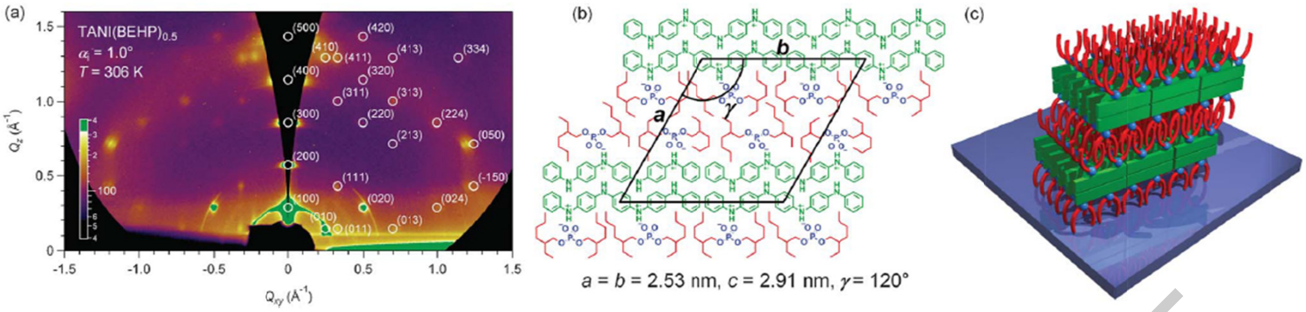

Figure 14. (a) GIXS pattern for the TANI(BEHP)$_{0.5}$ film (b) interpretation of the contents of the hexagonal TANI(BEHP)$_{0.5}$ unit cell in the ab- plane; and (c) schematic of the TANI(BEHP)$_{0.5}$ packing structure showing the orientation relative to the underlying substrate. Reproduced from [132]. With permission from Royal Society of Chemistry.

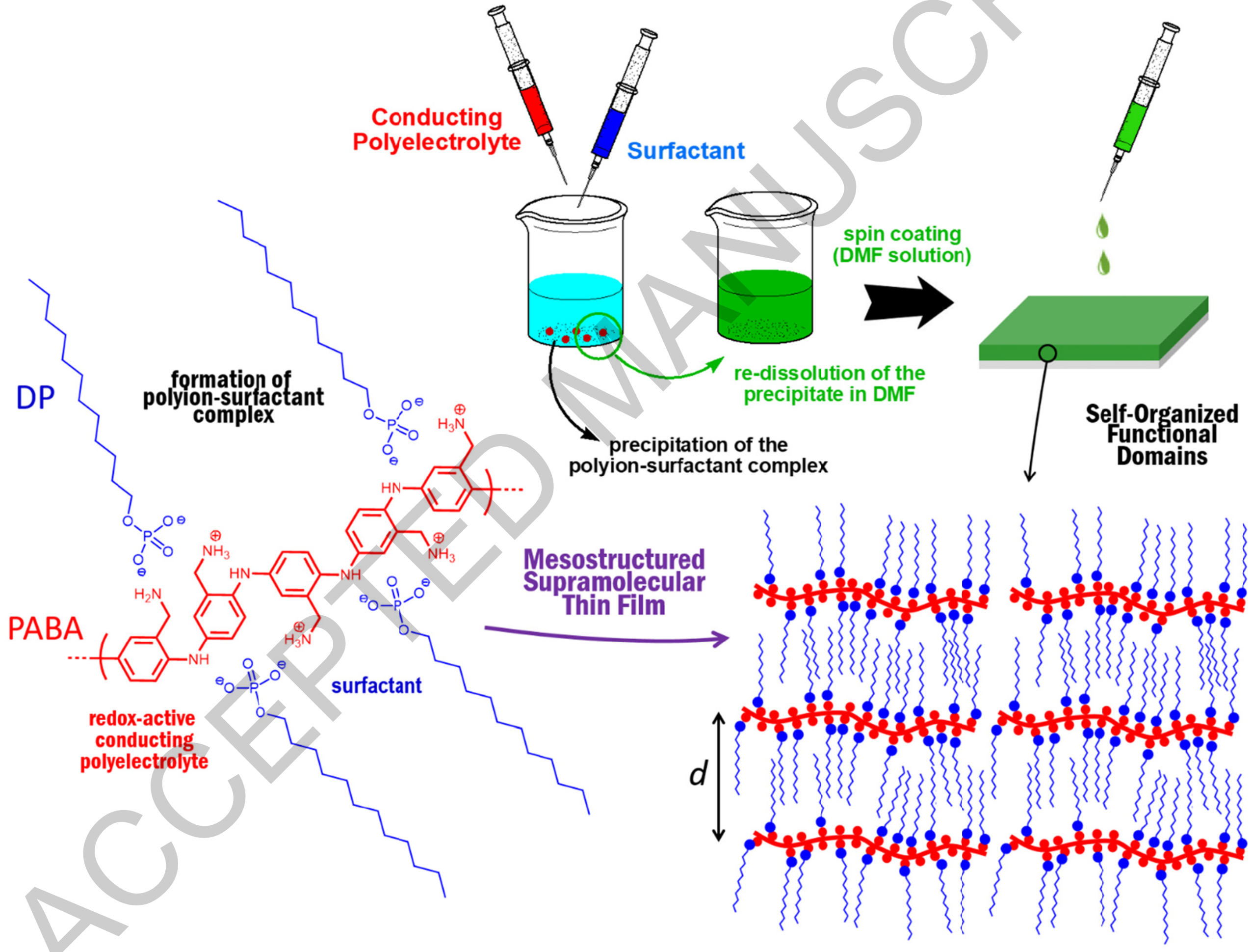

Figure 15. Schematic depiction of the preparation procedure and structure of the poly(3-aminobenzylamine) (PABA) and monododecyl phosphate (DP) films. Reproduced from [149]. With permission from Royal Society of Chemistry.

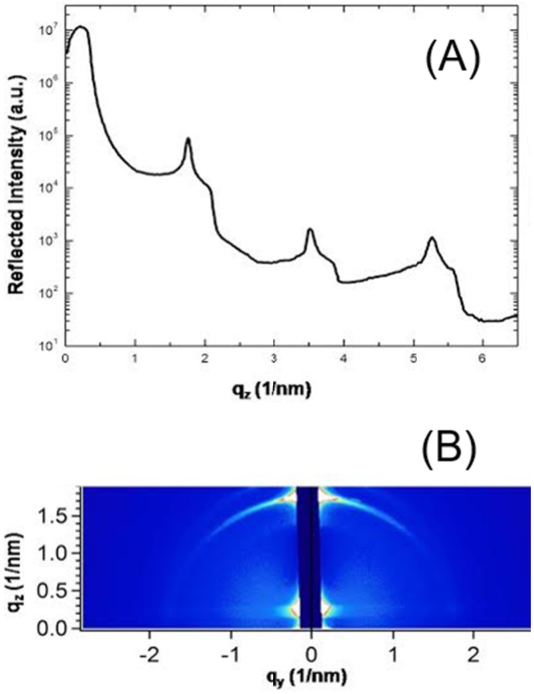

Figure 16. (A) X-ray reflectivity (XRR) and (B) grazing-incidence small-angle X-ray scattering (GISAXS) characterization of 1:5 PABA–DP films. Reproduced from [149]. With permission from Royal Society of Chemistry.

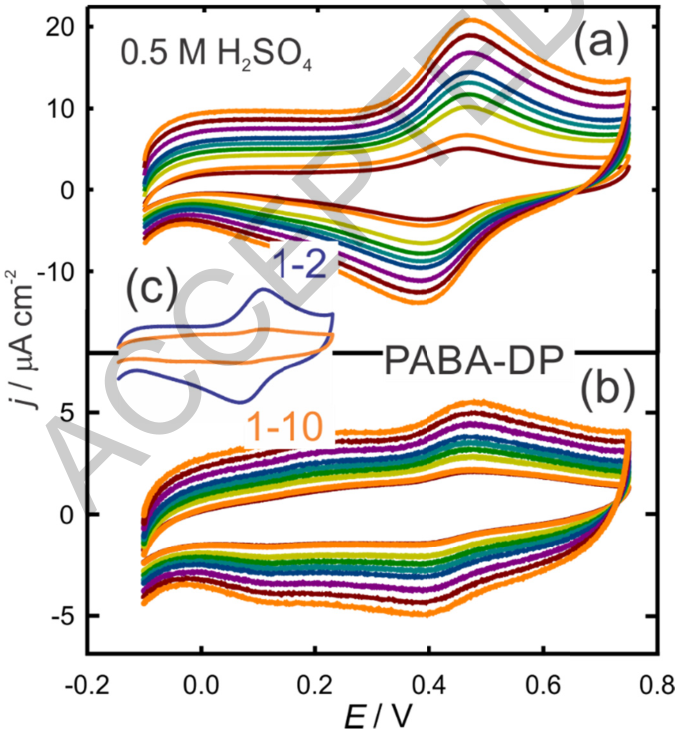

Figure 17. Voltammetric response of a PABA–DP-coated gold electrode at different sweep rates from 10 to 120 mV s^{-1} in sulfuric acid solution. (a) PABA–DP 1:2, (b) PABA–DP 1:10. (c) Comparison of the

voltammograms for both electrodes at the same scale. Reproduced from [149]. With permission from Royal Society of Chemistry.

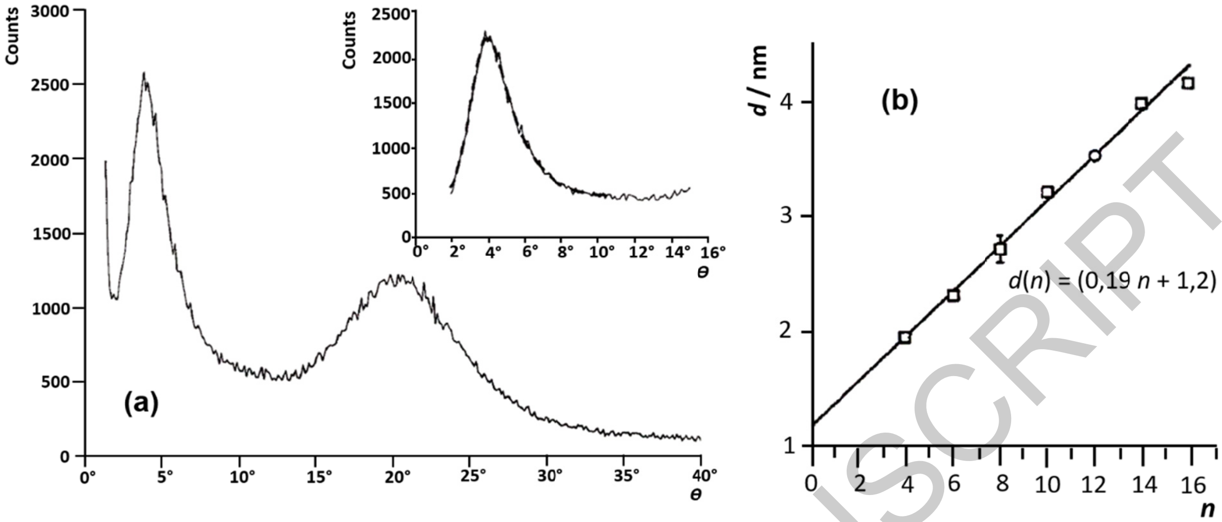

Figure 18. (a) X-ray diffraction pattern of polypyrrole-octanesulfonate. The inset shows a comparison of the fitted theoretical line shape with the experimental one. (b) Plot of the fitted d-values of the first X-ray diffraction peak for a series of polypyrrole sulfates versus number of carbon atoms, *n*, in one n-alkyl chain of the incorporated anionic surfactant. Reproduced from [151]. With permission from VCH-Wiley.

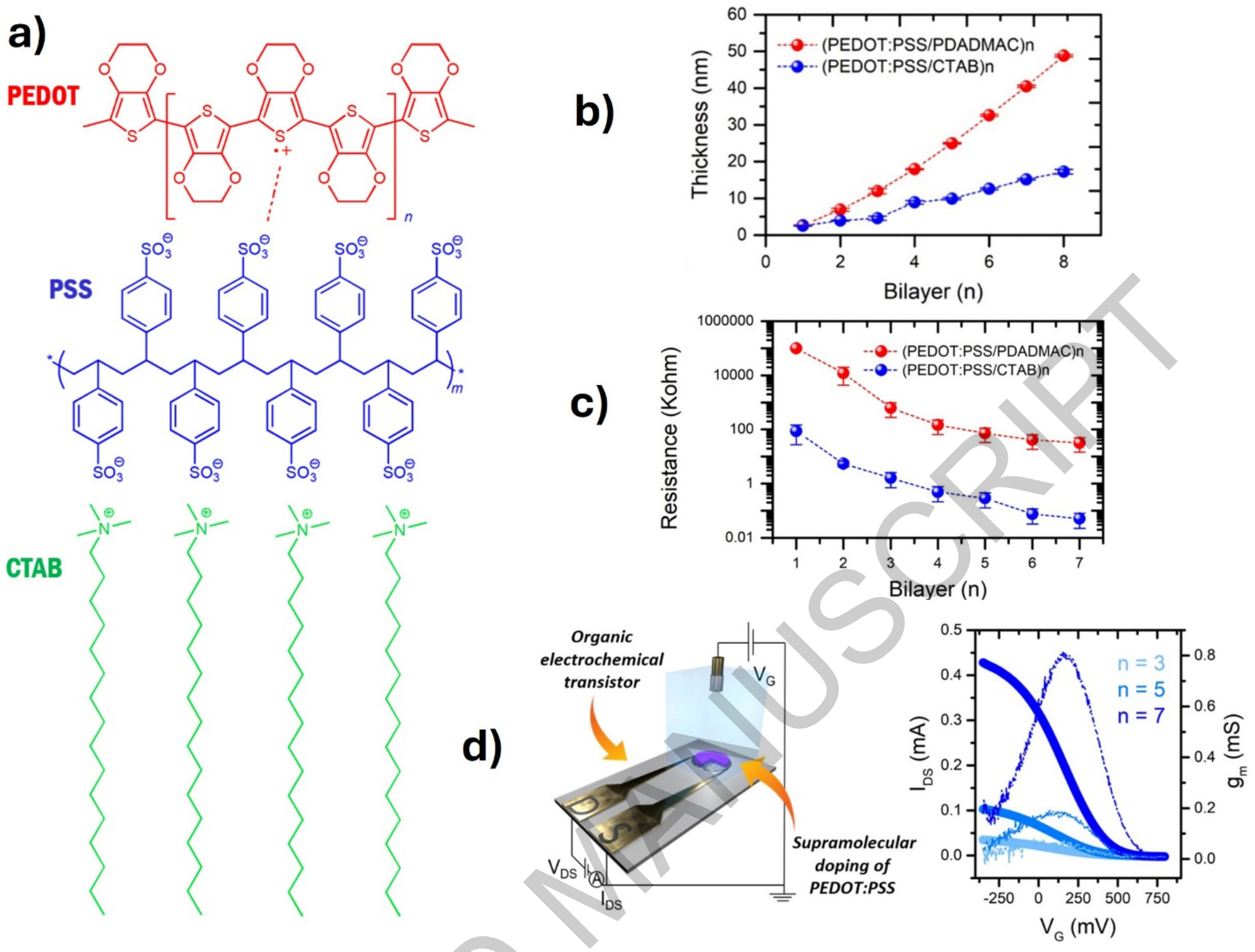

Figure 19. a) Schematic representation of the structure of PEDOT:PSS/CTAB self-assembled complex. **b)** Film thickness obtained by ellipsometry of $(PEDOT:PSS/PDADMAC)_n$ (red) and $(PEDOT:PSS/CTAB)_n$ (blue) assemblies as a function of the number of LbL cycles (*n*). **c)** Electrical resistance of (PEDOT:PSS/PDADMAC)n (red) and (PEDOT:PSS/CTAB)n (blue) assemblies. **d)** Transfer curves (solid line, left-Y) and transconductance curves (dashed line, right-Y) for $(PEDOT:PSS/CTAB)_n$ organic electrochemical transistors (OECTs). Reproduced from [159]. With permission from American Chemical Society.

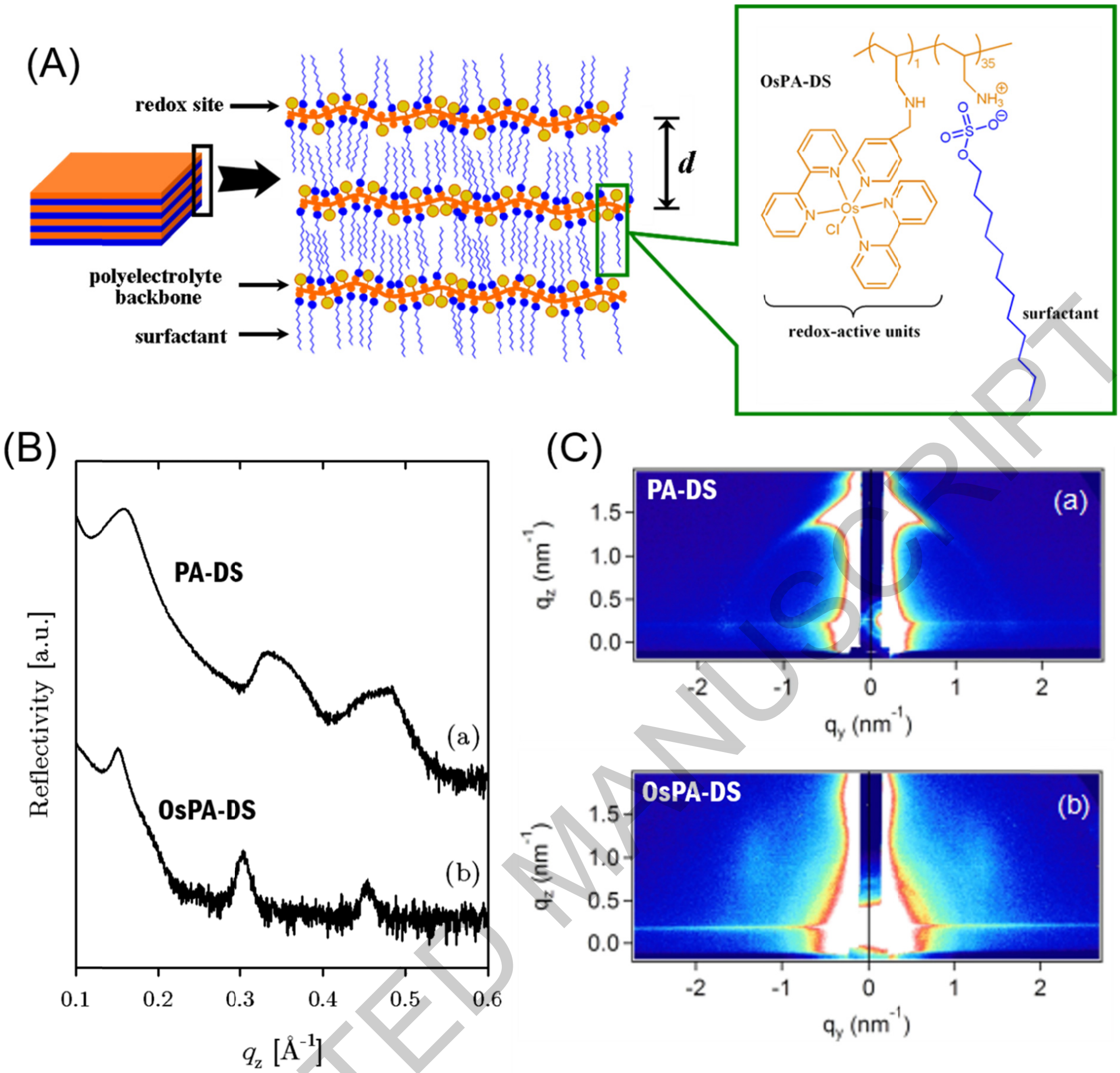

Figure 20. (A) Schematic of the different layers constituting the lamellar assembly: ionic layers correspond to the polyelectrolyte and dodecyl sulfate head groups, whereas the alkane layers correspond to interdigitated hydrophobic tails (dodecyl groups). (B) X-ray reflectivity data for (a) PA-DS and (b) OsPA-DS films measured under ambient conditions. (C) GISAXS patterns corresponding to (a) PA-DS and (b) OsPA-DS films measured at under ambient conditions. Films were spin-coated on Si(100) substrates. Reproduced from [166]. With permission from Elsevier BV.

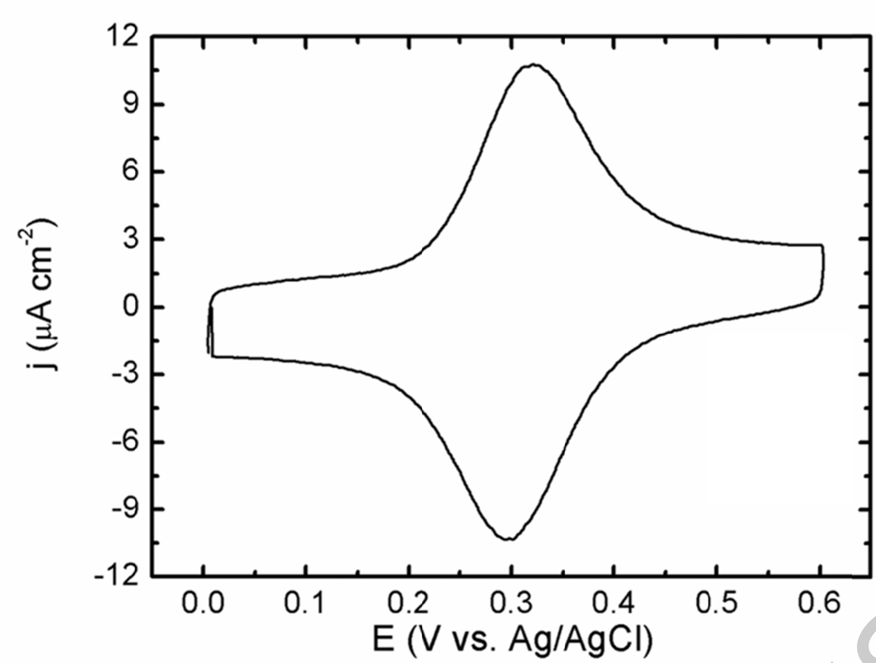

Figure 21. Cyclic voltammetry of the OsPA-DS film on ITO at 100 mV s^{-1} in 20 mM Tris-HCl buffer, pH 7.4 and 0.1 M KNO_3. Film thickness: 150 ± 20 nm. Reproduced from [166]. With permission from Elsevier BV.

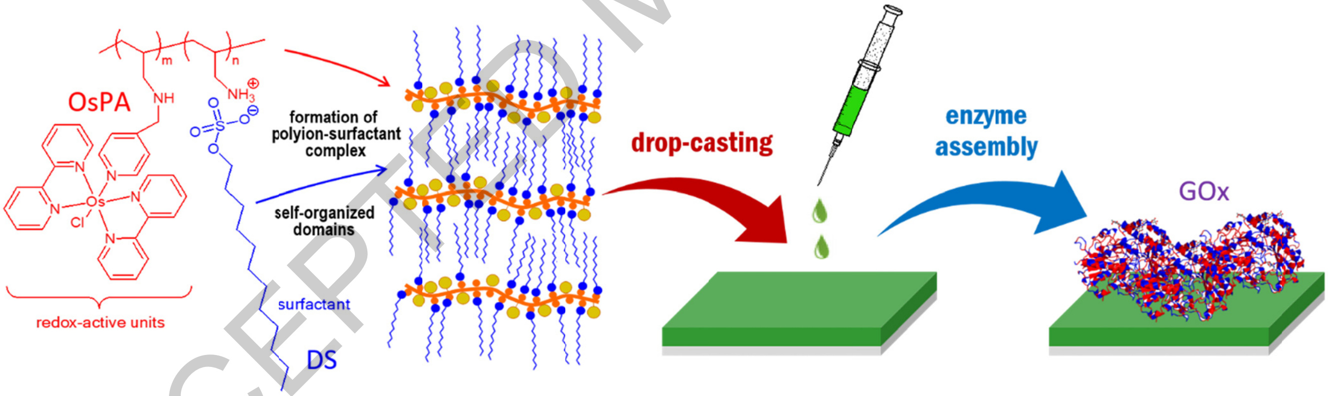

Figure 22. Representation of the preparation procedure of (OsPA–DS/GOx) films.

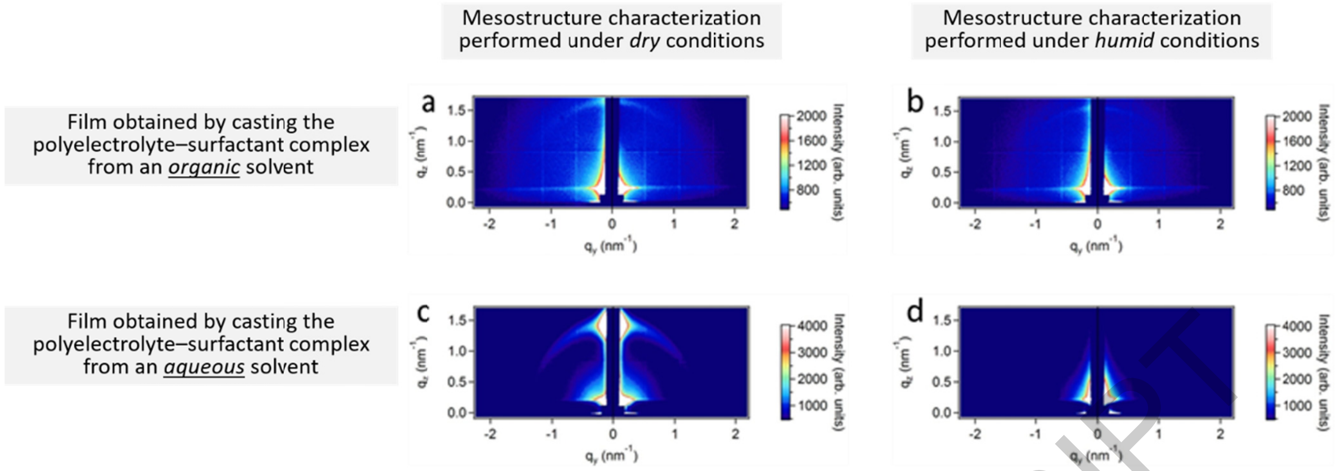

Figure 23. GISAXS patterns obtained from OsPA-DS$_{org}$ (a and b) and OsPA-DS$_{aq}$ (c and d) films measured under 0% (a and c) and 95% (b and d) relative humidity conditions. Films were spin-coated on Si(100) substrates Reproduced from [171]. With permission from Elsevier BV.

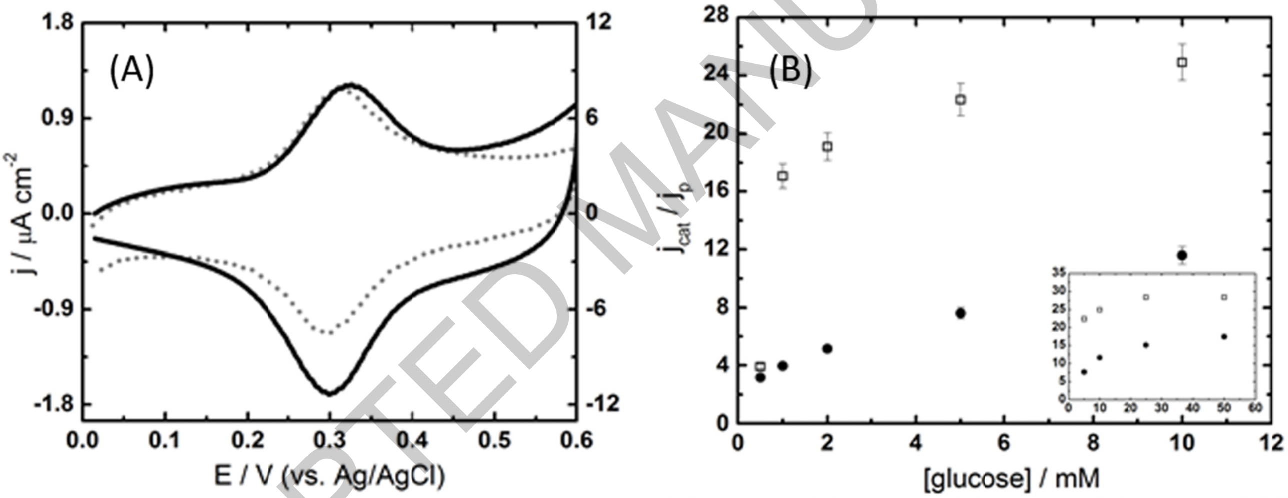

Figure 24. (A) Cyclic voltammogram at 10 mV s^{-1} for OsPA–DS$_{aq}$ (black line, current scale on the right y-axis), and OsPA–DS$_{org}$ (dotted line, current scale on the left y-axis). (B) Current response of OsPA–DS$_{aq}$ (white squares) and OsPA–DS$_{org}$ (black circles) to low glucose concentrations. Inset: the extended plot until 50 mM glucose concentration. Reproduced from [171]. With permission from Elsevier BV.

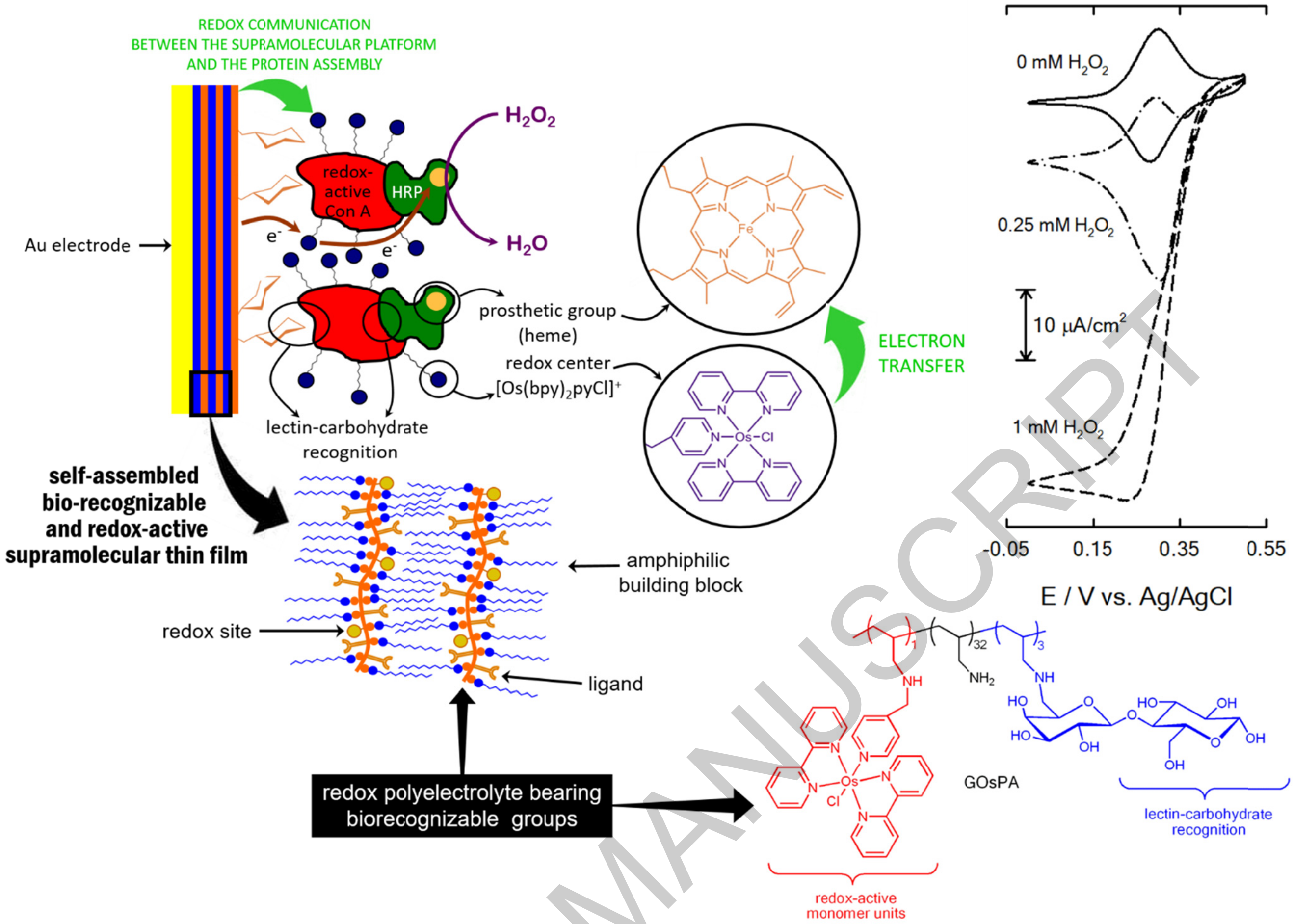

Figure 25. Simplified schematic of the H_2O_2-responsive interfacial supramolecular architecture. Redox-active Con A and HRP are spontaneously assembled via molecular recognition processes onto the redox-active glycopolyelectrolyte−surfactant supramolecular thin film. The figure displays the constituting building blocks participating in the generation of the biolectrochemical signal in the presence of hydrogen peroxide as well as a simplified view of their organization in the interfacial architecture. Source: Cortez *et al. Anal. Chem.* 2013, 85, 2414. Reproduced with permission of American Chemical Society. The figure also includes cyclic voltammograms describing the electrochemical response of gold electrode modified with a GOsPA-DS/Os-ConA/HRP assembly in the absence and in the presence of H_2O_2. Reproduced from [177]. With permission from Royal Society of Chemistry.

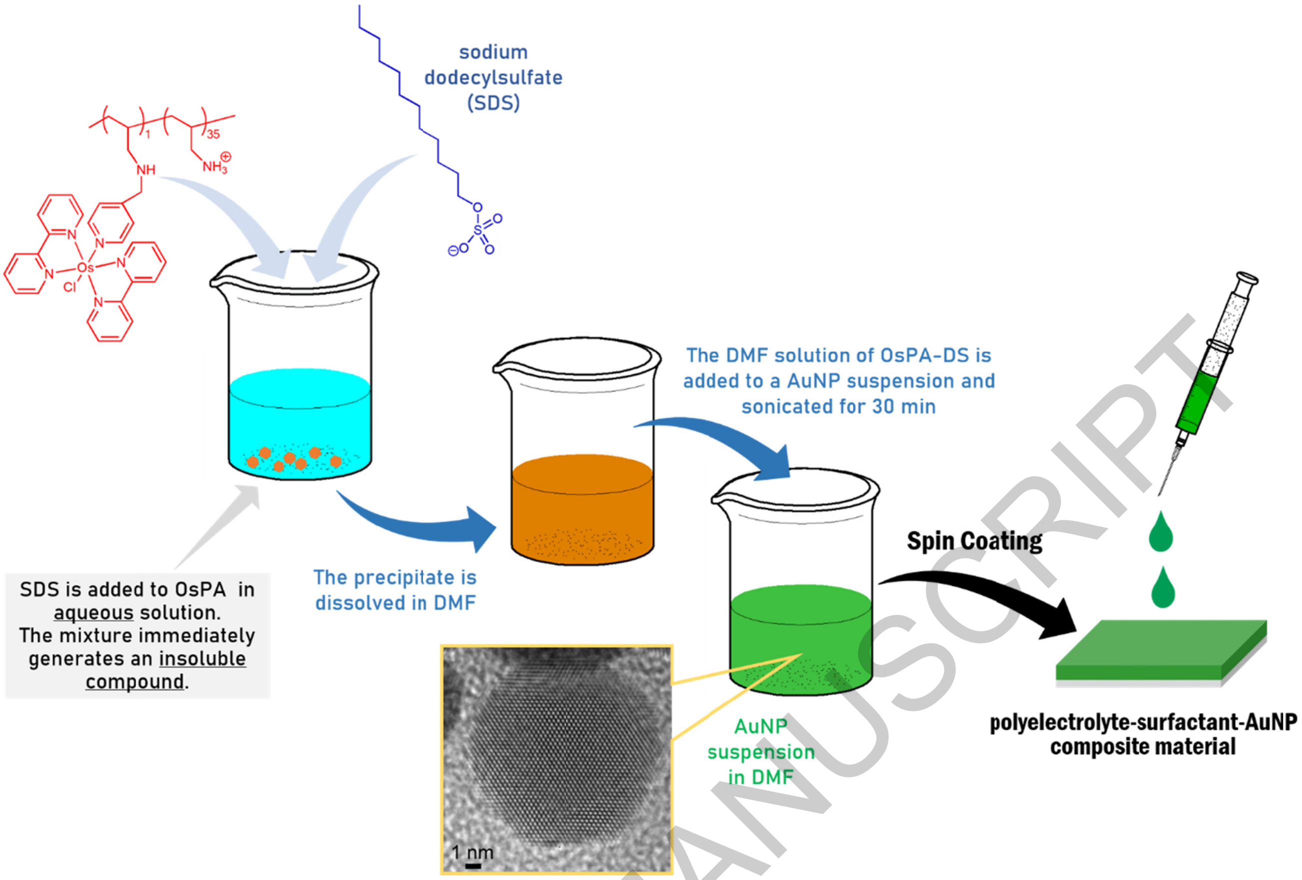

Figure 26. Representation of the preparation procedure of OsPA-DS-AuNP films.

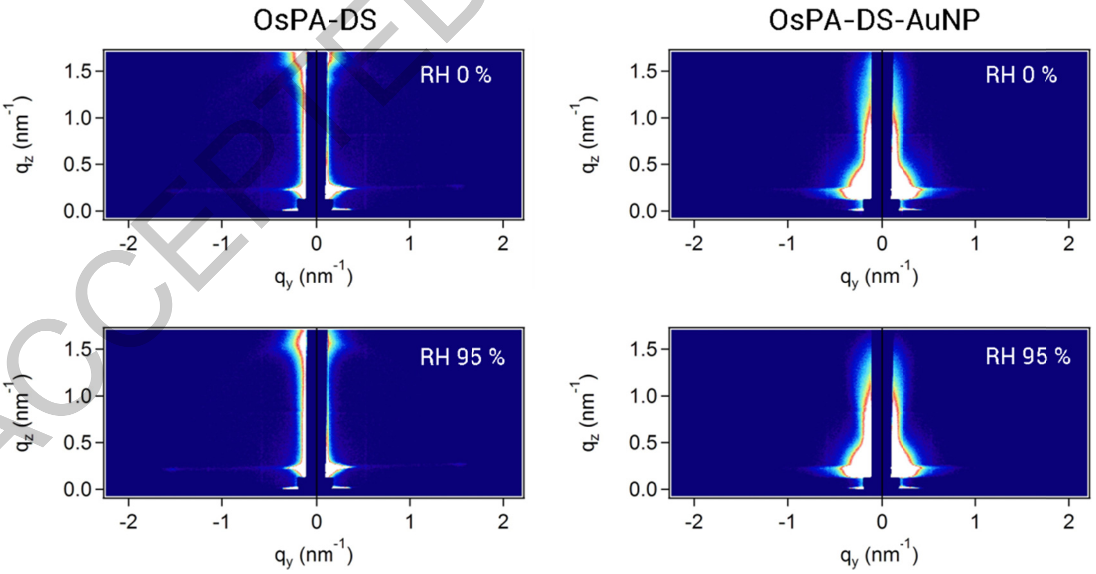

Figure 27. GISAXS patterns obtained from (left) OsPA-DS and (right) OsPA-DS-AuNP films measured under low (top) and high (bottom) humidity conditions. Films were spin-coated on Si(100) substrates. Reproduced from [183]. With permission from VCH-Wiley.

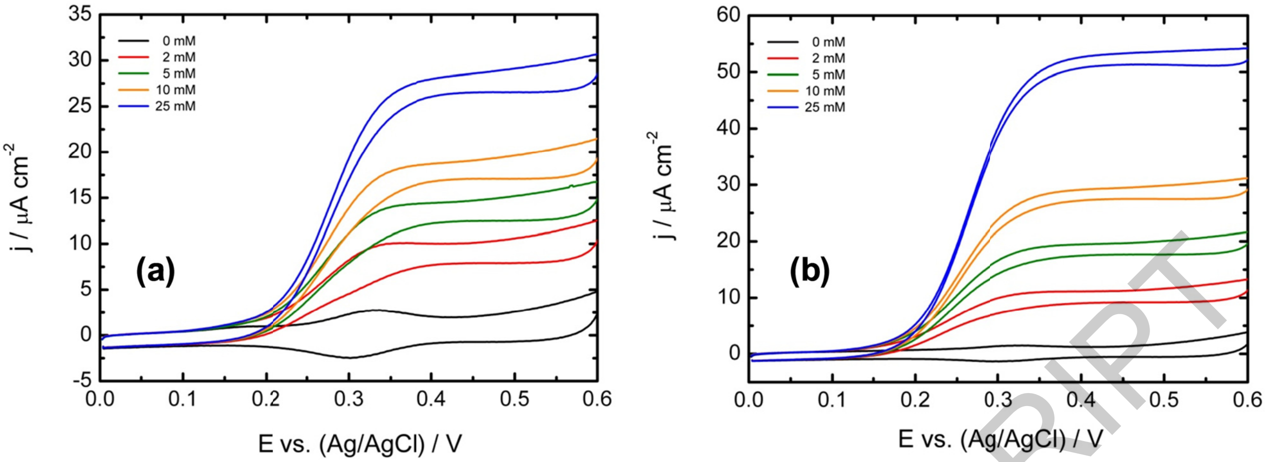

Figure 28. Bioelectrocatalytic response of composite platforms in the presence of increasing amounts of glucose: (a) Au/OsPA-DS/GOx electrode, (b) Au/OsPA-DS-AuNP/GOx electrode. Reproduced from [183]. With permission from VCH-Wiley.

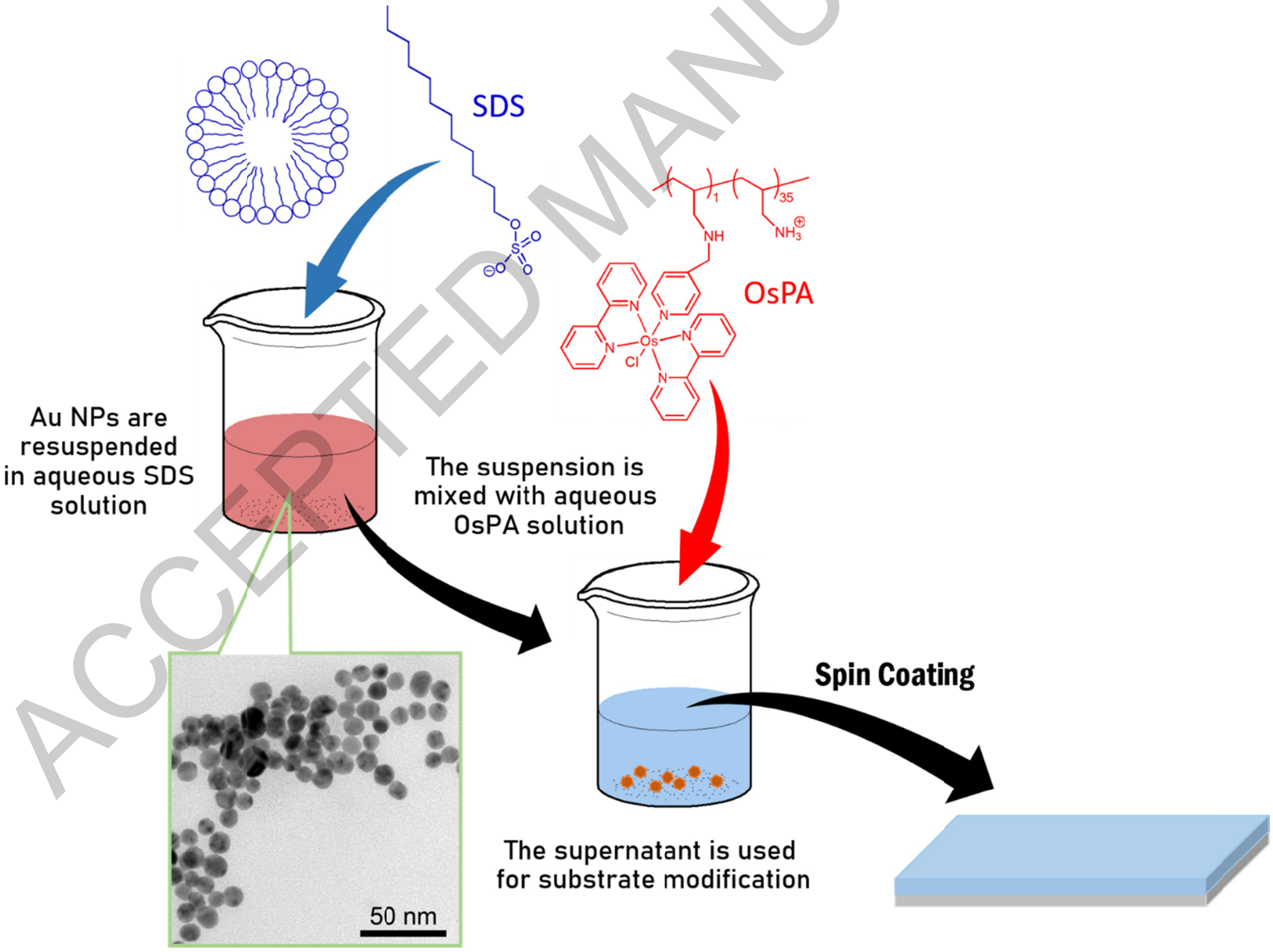

Figure 29. Representation of the preparation procedure of OsPA-DS-AuNP films in aqueous solvents.

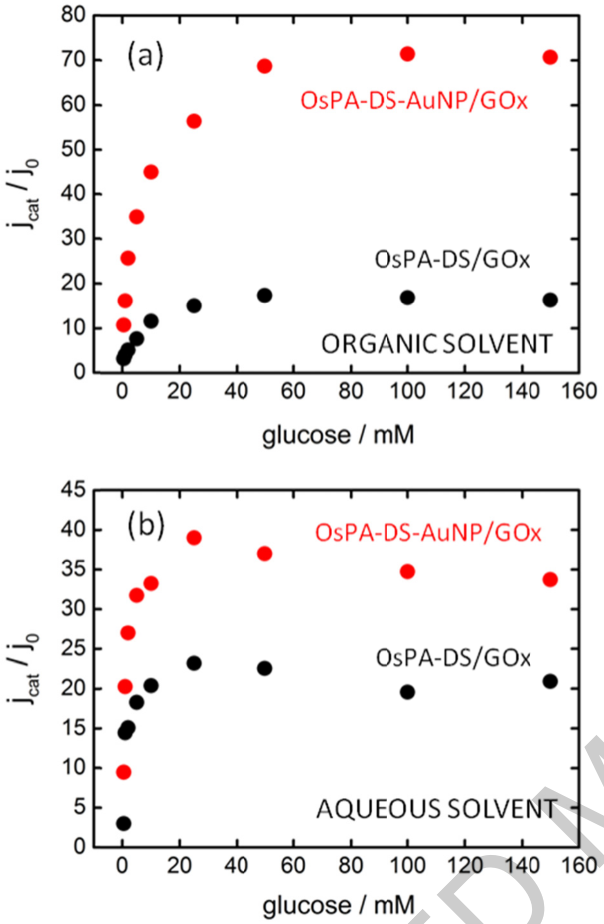

Figure 30. Representation of j_{cat}/j_0 ratio as a function of glucose concentration (j_{cat} = current density observed in presence of glucose and j_0 =current density observed in absence of glucose). Panel (a) depicts the bioelectrocatalytic response of electrodes modified with OsPA-DS-AuNP/GOx nanocomposites and OsPA-DS/GOx assemblies cast from organic solutions. Panel (b) depicts the bioelectrocatalytic response of electrodes modified with OsPA-DS-AuNP/GOx nanocomposites and OsPA-DS/GOx assemblies cast from aqueous solutions. Reproduced from [184]. With permission American Chemical Society.

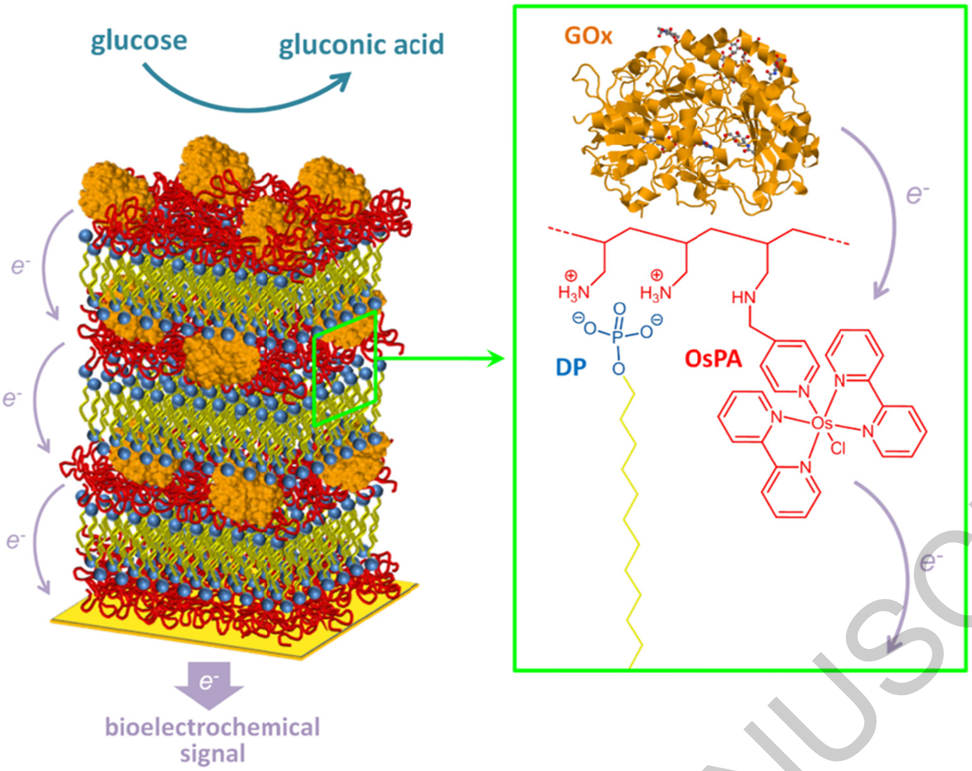

Figure 31. Schematic depiction of multicomposite OsPA/DP/OsPA/GOx multilayers.

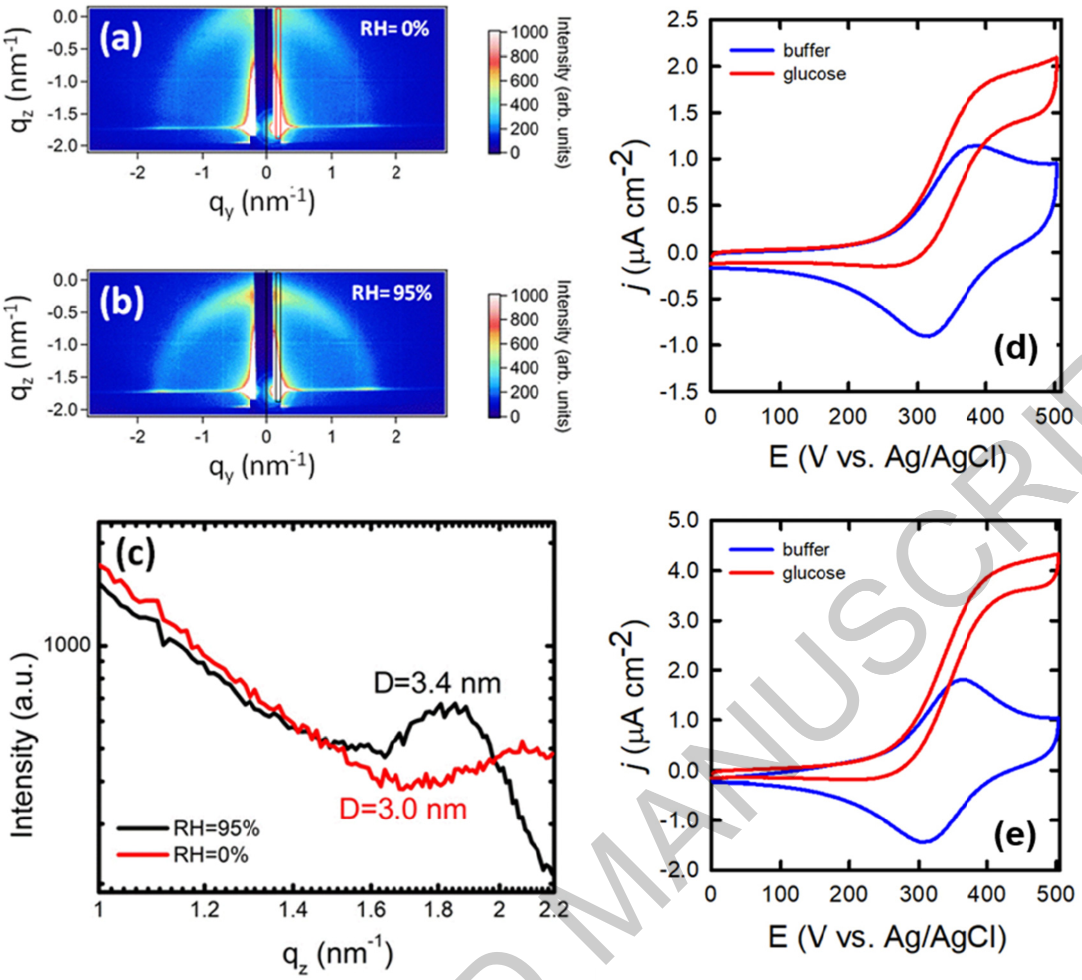

Figure 32. GISAXS patterns corresponding to a (OsPA/DP/OsPA/GOx)$_5$ multilayer self-assembled on a silicon substrate measured at: (a) RH ~ 0% and (b) RH ~ 95%. (c) Out-of-plane scattering profiles from the GISAXS patterns of (OsPA/DP/OsPA/GOx)$_5$ multilayers obtained under different humidity conditions. Cyclic voltammograms corresponding to: (d) (OsPA/DP/OsPA/ GOx)$_5$ and (e) (OsPA/DP/OsPA/GOx)5/OsPA. The blue trace refers to voltammetric measurements performed in the absence of glucose whereas the red trace refers voltammetric measurements performed in the presence of 50 mM glucose. Supporting electrolyte: 100 mM Tris–HCl buffer +0.1 M NaCl (pH 7.4). Reproduced from [185]. With permission Royal Society of Chemistry.