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Metal Ion-Linked Molecular Multilayers on Inorganic Substrates: Structure and Applications

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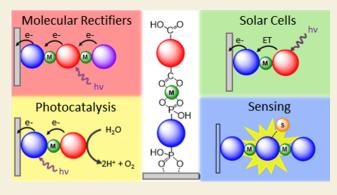


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ABSTRACT: Metal ion-linked multilayers have emerged as a simple and modular means of assembling molecular components on an inorganic substrate. The choice of molecules, based on their excited state energies and redox potentials, has enabled the directional control of energy and electron transfer events for application in electrochromics, solar energy harvesting, molecular rectifiers, photocatalysis, and more. Here, we recount the more than 35-year journey of metal ion-linked multilayers and their transition from planar to mesoporous substrates and from homogeneous to heterogeneous multilayers. This includes showcasing the vast range of components (i.e., substrates, metal ions, and molecules), structural insights, and applications. We also highlight current limitations in our knowledge of and ability to



control these systems which must be overcome to realize the full potential of metal ion-linked multilayers.

KEYWORDS: multilayer, metal oxide, metal ion linked, energy transfer, electron transfer

1. INTRODUCTION

Nearly a century of theoretical and experimental work has underscored the importance of distance and orientation on intermolecular communication and its impact on photoinduced events like energy and electron transfer. 1,2 Its importance is arguably best exemplified in photosynthetic systems, where millions of years of evolution have optimized the structure of supramolecular assemblies to funnel excited states and redox equivalents to specific reaction centers.^{3,4} Progress has also been made on human generated assemblies that control molecular orientation and proximity via molecular crystals, covalent and metal organic frameworks, phospholipid bilayers, polymers, and more. 5-10 Self-assembly via metal ionlinked multilayers is a particularly appealing strategy because of their ease of preparation, versatility in component selection/ design, and control over structure, and they are assembled on an inorganic substrate which is useful in hybrid electronics, heterogeneous catalysis, sensing, and more. 11-13 The multilayers are prepared via a stepwise loading procedure (Figure 1a) where an inorganic substrate is first soaked in a solution containing a molecule having a surface binding motif and a geometrically opposed metal binding group (e.g., COOH, PO₃H₂). The monolayer films are then submerged in a solution containing a metal-linking ion (typically Zn²⁺ or Zr⁴⁺) followed by a second molecule (either the same or different), and so on. 14 The self-limiting nature of the binding process

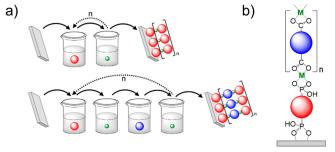


Figure 1. (a) The stepwise loading procedure for homogeneous (top) and heterogeneous (bottom) multilayers and (b) a general depiction of the multilayer assembly (molecule one is red, molecule two is blue, and the metal linking ion is green). Reproduced with permission from ref 14. Copyright 2020 Elsevier.

results in an n-layers thick film from n moleculelion cycles (Figure 1b).

Since their initial report in 1988,¹⁵ these metal ion-linked multilayers have been used in a range of applications including

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Figure 2. Proposed scheme of growth of 1,10-decanebisphosphonic acid-Zr⁴⁺ multilayers on planar silicon wafers. Reproduced with permission from ref 15. Copyright 1988 American Chemical Society.

solar energy conversion, electrochromism, catalysis, and more (vida infra). Although seemingly disparate, all of these applications rely on interfacial electron and energy transfer events which are dictated by molecular distance and orientation. Consequently, the aim of this review is to recount the ~35-year history of metal ion-linked multilayers with an emphasis on the structural insights gained and the application of these assemblies. It will progress from the seminal research on planar substrates (Section 2) to the more recent work on mesoporous metal oxide films (Section 3). Finally, we close with a summary of progress and suggest some gaps in knowledge that are yet to be filled to realize the full potential of metal ion-linked multilayer films.

2. METAL ION-LINKED ASSEMBLIES ON PLANAR SURFACES

2.1. Introduction of Metal Ion-Linked Multilayers

In 1988, Mallouk and co-workers were the first to report a metal ion-linked multilayer film as depicted in Figure 2. ¹⁵ The films were prepared by exposing a silicon substrate to a solution containing a silanol derivatized alkyl phosphonate molecule. The substrate was then repeatedly exposed to solutions containing ZrOCl₂ and 1,10-decanebisphosphonic acid. The film growth was monitored by ellipsometry, and the increase in thickness for the treatment cycle was found to correspond with the length of the alkylphosphonic acid molecule. In the absence of metal ion soaking, no growth was observed supporting the model depicted in Figure 2. The metal ion-linked multilayer films were generally more robust and reproducible than previously reported noncovalent ^{16,17} or siloxy multilayers. ¹⁸

Subsequent work by Mallouk and co-workers focused on testing the versatility and utility of the layer-by-layer assembly strategy with different substrates (e.g., fumed silica powder, gold), molecules, and metal ions (Zn²⁺, Fe²⁺, Cu²⁺). 19-26 They used X-ray photoelectron spectroscopy, attenuated total reflectance infrared spectroscopy (ATR-IR), AFM, solid-state NMR, and thin-film X-ray measurements to further support the coordination scheme, film thickness, and relatively wellordered, layered structure of the film. Based on the ellipsometry film thicknesses and X-ray structure of related alkylphosponate-divalent metal ion crystals, Mallouk and coworkers proposed that the chain axis of the molecules was tilted by 34° relative to surface normal (Figure 3).²³ They also demonstrated that adsorption of molecules like CO2 and ammonia in the multilayer enabled the use of metal ion-linked multilayers in quartz crystal microbalance sensors.^{27,28}

2.2. The First Photoactive Multilayers

Following the discovery that long-lived photoinduced charge separation could be achieved in layered zirconium viologen

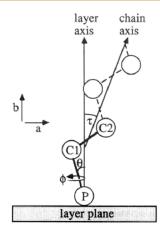


Figure 3. Proposed alkyl chain tilt angle (τ) for a divalent metal phosphonate multilayer. Reproduced with permission from ref 23. Copyright 1993 American Chemical Society.

phosphate materials/thin films^{29,30} and the existence of excited state quenching in multilayers by Ungashe et al.,³¹ Thompson and co-workers began studying the growth and the photochemical properties of metal ion-linked multilayers on inorganic substrates. Using AFM to monitor thin film growth, the team noted that initially there was an inhomogeneous distribution of the surface bound alkylphosphonate molecules. However, subsequent alkylphosphonate treatment and multilayer growth dramatically increased the uniformity of the film, leading the authors to exclaim "These Things Grow Darned Flat!"³²

Alternating layers of photoactive and electroactive molecules like methylviologen and phenylenediamine bisphonsphonic acids on gold and ITO substrates enabled the use of these multilayers for photoelectrochemical measurements. 33,34 Upon excitation, electron transfer from the phenylenediamine donor layer to the methylviologen acceptor layer was followed by electron transfer to a Eu³⁺ mediator in solution, resulting in a sustained photocurrent from the film that was more than 10 times greater than single component multilayer films (e.g., methylviologen only). Worth noting is that the direction of electron flow could be reversed by switching the spatial ordering of the donor and acceptor layers. However, due to the low absorption cross section and high energy absorption of the molecules, the overall incident photon-to-current efficiency (IPCE) was on the order of 0.1%. 34 In line with prior work, 31 the incorporation of porphyrin molecules into the multilayer on gold substrates (Figure 4) increased visible absorption and significantly improved the photocurrent generation over prior devices.35

Subsequently, the team also demonstrated that the zirconium- and hafnium-viologen phosphonate layers could

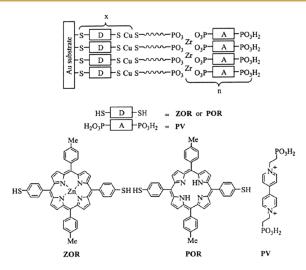


Figure 4. Structure of the porphyrins and the viologen derivatives (bottom) that were incorporated into the multilayer photoelectrode (top). Reproduced with permission from ref 35. Copyright 2002 American Chemical Society.

be grown off of platinum colloids for photocatalytic hydrogen ³⁶ or hydrogen peroxide ³⁷ production.

2.3. Redox Active Ruthenium Polypyridyl Multilayers

In the early 2000s, Haga and co-workers began their efforts incorporating ruthenium(II) and osmium polypyridyl complexes into zirconium-phosphonate multilayer films to control the directionality of interfacial electron transport (Figure 5). 38,39

Cyclic voltammograms of the films exhibited nonequivalent anodic and cathodic currents depending on the energetic/redox ordering of the species, indicating that multilayers can potentially serve as a rectifying interface. Incorporation of redox active linking ions like Fe^{2+} increased the electron transport capabilities of the film via both hopping and tunneling mechanisms.

XPS, ellipsometry, and TOF-SIMS measurements indicated that multilayer growth was initially limited to 6–7 layers, which the authors attribute to the large tilt angle creating a domain boundary as depicted in Figure 6.⁴¹

However, through variation in the film loading conditions, Haga and co-workers increased the monolayer loading and film uniformity, enabling the formation of at least 65 monolayers.⁴² The thicker films exhibited pseudocapacitor behavior with

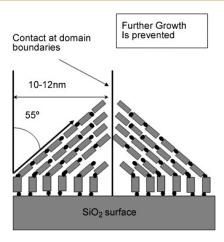


Figure 6. Drawing of the proposed thickness saturation mechanism of the multilayer assemblies. Reproduced with permission from ref 41. Copyright 2009 Elsevier.

excellent cycling stability and a capacitance of 92.2 F g⁻¹ at a current density of 10 μ A cm⁻², effectively demonstrating the promise for these multilayer assemblies for electrochemical energy storage.

2.4. Additional Planar Multilayers

The above discussion focused on the contributions of Mallouk, Thompson, and Haga, but there are many additional reports describing the assembly, characterization, and application of metal ion-linked multilayers. Aside from the more common metal-phosphonate layering scheme, there are several reports that rely on the assembly of Co²⁺, Ru³⁺, Fe²⁺, and other transition metal coordination complexes as the multilayer linking motif switches with some examples shown in Figure 7.

Additional structural insights have been provided by measurements like grazing-incidence small-angle scattering and support the proposed alternating organic-metal ion layered structure. Structure. Likewise, second harmonic generation measurements show that better multilayer film ordering is observed with more rigid linkers, Structure, thin disorder increases with adsorption of additional layers. These films have also been applied in a range of applications including molecular wires, thin film transistors, the photocurrent generation, electrochromics, and photocatalytic hydrogen generation and for hindering aggregation/emission quenching.

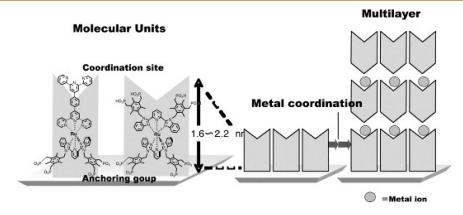


Figure 5. Ruthenium polypyridyl complexes and schematic of the multilayer assembly. Reproduced with permission from ref 39. Copyright 2007 Elsevier.

Figure 7. Examples of metal ion-linked multilayer assemblies. Reproduced with permission from ref 39. Copyright 2007 Elsevier.

3. METAL ION-LINKED ASSEMBLIES ON MESOPOROUS SURFACES

In 2013, metal ion-linked multilayers on mesoporous, nanocrystalline metal oxide films were reported for the first time. ⁵⁹ The high surface area of the nanoparticle metal oxide film enabled dramatically increased molecular loading density and absorption cross-section increased by more than 2 orders of magnitude (Figure 8). ¹⁴

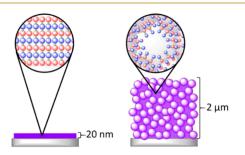


Figure 8. Metal ion-linked multilayer assemblies on planar (left) and nanoparticle (right) films with molecules in blue and red and linking ion in green. Reproduced with permission from ref 14. Copyright 2020 Elsevier.

This planar-to-mesoporous transition is analogous to that of dye-sensitized solar cells (DSSCs), whose dye-sensitized mechanism was first reported on planar surfaces in 1972, 60 but its practical utility for solar energy harvesting dramatically increased with the introduction of mesoporous metal oxides by O'Regan and Grätzel in 1991. 61 Similarly, the assembly of metal ion-linked multilayers on mesoporous metal oxides not only increased their light harvesting capabilities, but also dramatically increased the ease of steady-state and time-resolved spectroscopic monitoring of energy and electron transfer dynamics in the films. Consequently, the use of mesoporous substrates led to a rebirth in interest in metal ion-

linked multilayers for use in applications in solar energy conversion, photocatalysis, electrochromism, and more (*vida infra*). In this section, we recount various examples of metal ion-linked multilayers, structural insights, and applications by progressing stepwise through metal ion-functionalized monolayers (Section 3.1), bilayers (Section 3.2), trilayers (Section 3.3), and beyond (Section 3.4).

3.1. Metal Ion Functionalized Monolayers

Molecular monolayers on mesoporous metal oxide films (MO_x) have been extensively investigated for use in DSSCs, and that progress has been reviewed elsewhere. Here, we limit our discussion to monolayer and metal ion loading in the context of its impact on structure, subsequent multilayer formation, and applications.

Molecules have been coordinatively bound to metal oxide surfaces via various functional groups including pyridine, hydroxamic, and silane groups, but by far the most common are carboxylate (–COOH) and phosphonate (–PO $_3$ H $_2$). $^{63-66}$ The surface loading is typically monitored using UV–vis spectroscopy, 14,62 but for molecules whose absorption is masked by the glasslMO $_x$ substrate, techniques like ATR-IR 59,67,68 and ICP-MS 69 have been used to quantify loading. Both the position of the functional group and the surface binding mode/number of groups have been shown to impact molecular orientation, electron injection dynamics, cross surface energy/electron transfer, and other properties. $^{70-72}$

The proposed binding modes for -COOH and $-\text{PO}_3\text{H}_2$ on MO_x are shown in Figure 9.⁶⁴ Differentiating between these binding modes has turned out to be a surprisingly challenging task. Techniques like ATR-IR, polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS), X-ray photoelectron spectroscopy (XPS), and others generally suggest that molecules usually favor a multidentate binding mode, with the binding mode dependent on the solvent, nature of the molecule, and loading condition (e.g., temperature, time, bubble loading). The solution of the solvent of the molecule, and loading condition (e.g., temperature, time, bubble loading). The solution of the solvent of

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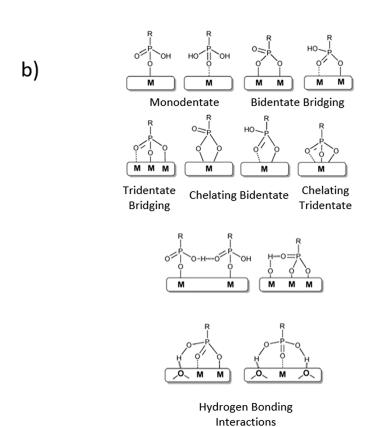


Figure 9. Proposed surface binding modes of -COOH (a) and -PO₃H₂ (b) on metal oxide surfaces. Reproduced with minor modifications with permission from ref 64. Copyright 2014 Wiley-VCH.

ments indicate inhomogeneity in the binding and that some phosphonates may prefer a monodentate binding mode.^{67,78}

Interestingly, recent polarized visible attenuated total reflection measurements on –COOH and –PO₃H₂ functionalized anthracene dyes indicate that regardless of binding group or metal oxide identity (i.e., Al₂O₃, ZrO₂, TiO₂, ITO), the orientation of the molecules relative to surface normal was the same.⁷⁹ This suggests that at least in some cases the coordination mode at the surface has less impact on molecular orientation than intermolecular interactions in the monolayer.

Crucial to the formation of metal ion-linked multilayers is geometrically opposed metal ion binding groups for subsequent ion loading. In terms of linking ions, similar to the planar multilayers (*vida supra*), Zr⁴⁺ and Zn²⁺ are the most common choice, but Cd²⁺, La³⁺, Sn⁴⁺, Cu²⁺, Fe²⁺, and Mn²⁺ have also been used to generate multilayers. ^{80–82} The binding of the metal ion has been probed using XPS, ICP-MS, and ATR-IR measurements, ^{69,81,83,84} but the specific coordination environment around the metal linking ion and its impact on the structure of the multilayer is not yet well understood. Regardless, it is known that the choice of metal ion can impact subsequent layer addition, excited state quenching, energy/

electron transfer dynamics, and also performance in solar energy conversion devices.

For example, it was first shown that Hg^{2+} ion coordination to the thiocyanates of ruthenium polypyridyl dyes (i.e., N3, N719, etc.) can impact hole percolation, recombination/regeneration kinetics, device performance, and the absorption energy of the dye. The latter change was effectively used as a colorimetric probe for Hg^{2+} ions when compared to Pb^{2+} , Cd^{2+} , Zn^{2+} , and Fe^{2+} 85

Subsequently in 2016, Ogunsolu et al. observed that even prior to multilayer formation, the coordination of Zr^{4+} ions to a phosphonate N3 dye equivalent increased the open circuit voltage $(V_{\rm OC})$ of a DSSC relative to the dye only, which was attributed to slowed recombination dynamics. In a follow-up study varying the identity of the metal ion (i.e., Zr^{4+} , Zn^{2+} , Cd^{2+} , La^{3+} , Sn^{4+} , Cu^{2+} , Fe^{2+} , and Mn^{2+}), the team suggested that electrostatic interaction with the redox mediator may be dictating the change in recombination. However, their subsequent study changing the charge of the redox mediator suggested that the size of the metal ion, more so than the charge, may be responsible for influencing recombination dynamics and DSSC performance. A similar impact by metal

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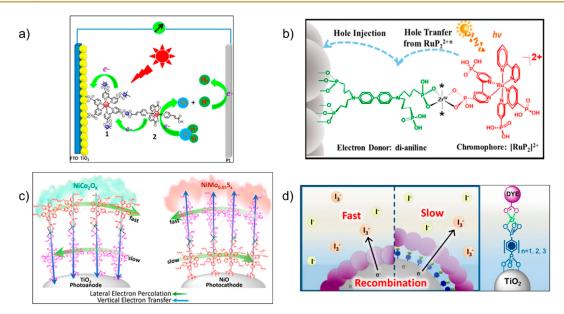


Figure 10. Metal ion-linked bilayers have been implemented in chromophore-catalyst assemblies (a), electron donor-chromophore assemblies (b), directional control of electron migration (c), and slowing recombination in dye-sensitized solar cells (d). (a) Reproduced with permission from ref 94. Copyright 2014 American Chemical Society. (b) Reproduced with permission from ref 101. Copyright 2017 American Chemical Society. (c) Reproduced with permission from ref 102. Copyright 2018 American Chemical Society. (d) Reproduced with permission from ref 104. Copyright 2015 American Chemical Society.

ion coordination was later observed by Kato, Kobayashi, and co-workers in hydrogen generation photocatalysis. 89,90

3.2. Bilavers

Following metal ion coordination, a second molecular layer can be adsorbed via the soaking procedure. For bilayer films, it is not uncommon to employ $-PO_3H_2$ functionalized molecules for the first layer and -COOH for the second layer 14,91 to avoid competitive desorption of the first layer by the more weekly binding -COOH molecule. 92

The first metal ion-linked bilayer film on a mesoporous metal oxide was composed of phosphonate functionalized ruthenium(II) polypyridyl complexes with Zr⁴⁺ linking ions on ZrO₂ and TiO₂ surfaces.⁵⁹ Film formation was monitored using UV—vis absorption, XPS, and ATR-IR. Time-resolved absorption and emission were used to demonstrate that energy and electron transfer could be directed toward or away from the surface depending on the ordering of the layers and their energetics. Since then, metal ion-linked bilayers have been implemented in a range of applications including control over electron transfer with some examples shown in Figure 10.

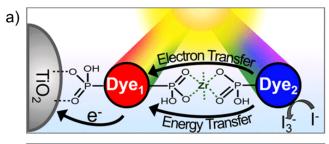
One of the first applications of a metal ion-linked multilayer on mesoporous oxides was the generation of chromophore-catalyst assemblies for water oxidation dye-sensitized photo-electrosynthesis cells (DSPECs). This assembly method circumvents the complex multistep synthesis of covalently linked chromophore-catalyst dyads as well as the surface area limitations of codeposition strategies. For example, Sun and co-workers used an assembly of a phosphonated Ru(II)-polypyridyl chromophore, Zr⁴⁺ linking ion, and a carboxylated Ru(II) catalyst (Figure 10a) to obtain a peak IPCE of 4.1% and a photocurrent density of ~0.48 mA cm⁻² for photocatalytic water oxidation. Beyond water oxidation, the bilayers have been used in hydrogen generation, and other DSPEC schemes. Beyond synthesis of multilayers in these DSPECs is enabled by photoexcitation and electron transfer by the chromophore, followed by rapid interlayer electron transfer

from the catalyst to chromophore (or vice versa) as observed by transient absorption spectroscopy. 98,99

The incorporation of electroactive, but not photoactive, electron transfer mediators in the assemblies has been used to mediate interlayer electron transfer from a water oxidation catalyst or between a chromophore and metal oxide surface (Figure 10b). In these cases, the mediator helps to geometrically separate the oxidized and reduced species and dramatically increases the charge separation lifetime. However, in at least one case, the geometric restriction imposed by the bilayer assembly sufficiently increased the separation between donor and acceptor such that electron transfer was completely inhibited. This further emphasizes the need to understand distance and orientation between molecules in the multilayers.

Bilayers also offer a means of influencing interassembly electron transfer events. For example, Meyer and co-workers demonstrated that the direction of interlayer and cross surface electron migration could be controlled depending on the order of assembly (Figure 10c). Alternatively, a photochemically and electrochemically inert phosphonated molecule can be used to spatially separate the dye molecule and the surface effectively slowing back electron transfer dynamics 103 and increasing $V_{\rm OC}$, but at the cost of slowed electron injection and lower photocurrents in a DSSC (Figure 10d). The intervening metal ion was also found to play a nontrivial role in excited state quenching and electron transfer. 80,82

Metal ion-linked assemblies have been used to facilitate light harvesting and energy transfer in dye-sensitized solar cells as depicted in Figure 11. For example, through the strategic choice of molecular components, it was demonstrated that bilayers could be used to increase broad band light absorption in DSSCs (Figure 11a).⁶⁸ In those devices, the chromophores were selected such that the lower energy absorber was adjacent to TiO₂, and the higher energy absorber was in the second layer. Consequently, it was energetically favorable for directional energy transfer toward the surface. Likewise, by placing the chromophore with the more positive oxidation potential



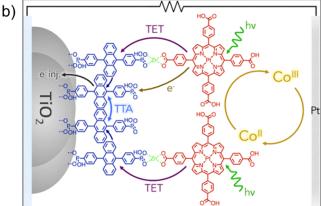


Figure 11. Metal ion-linked multilayers used in an energy transfer cascade (a) and TTA-UC (b) solar cells. (a) Reproduced with permission from ref 68. Copyright 2016 American Chemical Society. (b) Reproduced with minor modifications with permission from ref 109. Copyright 2017 American Chemical Society.

adjacent to the charge separation interface, an electron transfer cascade from the first layer to TiO₂, then the second layer to the first, and finally from the edox mediator to the second layer was observed by transient absorption spectroscopy. Similar energetic and redox alignment is used in many multilayer assemblies. For example, subsequent work showed that this type of energy cascade may be an effective means of harnessing low energy light in a singlet fission DSSC. ¹⁰⁵

In an alternative solar energy conversion scheme, it has been shown that metal ion-linked bilayers are an effective means of facilitating and harnessing photon upconversion via triplet—triplet annihilation (TTA-UC). ^{106,107} In TTA-UC, a sensitizer molecule absorbs low energy light, undergoes intersystem crossing, and then transfers the triplet excited state to an annihilator molecule. When two triplet annihilator molecules

are in proximity, the system can undergo TTA to generate a higher energy excited state that can either emit a photon, or in the case here, undergo charge separation and photocurrent generation. 108 In a TTA-UC bilayer assembly, the annihilator molecule is bound to a metal oxide surface, followed by a linking ion, and finally a sensitizer (Figure 11b). 109-111 Timeresolved emission and transient absorption measurements were used to elucidate the energy and electron transfer dynamics and kinetics in the assembly. 112 The bilayer effectively circumvents diffusion limited kinetics observed in solution, fixes the annihilators in proximity for triplet migration and TTA, charge separates the UC state before back energy transfer, and couples the assembly to a charge separation interface. Upconverted photocurrents of 0.158 mA cm⁻² have been observed in the bilayer device, which was orders of magnitude larger than those previously achieved with optically coupled schemes, but also only harnessed light in the visible portion of the solar spectrum. 109 Attempts to shift absorption to the near-IR have been successful but with a dramatic decrease in photocurrent partially due to back energy transfer losses. 113

To gain additional insight into the role of the bilayer structure on energy transfer dynamics and TTA, the position of the metal ion binding group was varied on both the annihilator^{70,114} and sensitizer molecules.¹¹⁵ In all cases, notable changes in the interlayer and cross-surface energy transfer rates were observed. Because the energy transfer event is dictated by the distance and relative orientation between the chromophores, additional insights into the structure of the bilayer were obtained by polarized, visible ATR measurements (p-ATR). 116-121 Briefly, the multilayer is assembled on a waveguiding glass slide coated with metal oxide that enables multiple internal reflections. The difference in attenuated absorption between transverse electric and transverse magnetic light provides insights into the orientation of the transition dipole moment of the chromophores relative to the surface normal. As can be seen in Figure 12a, the nature of the second molecule has minimal impact on the orientation of the first layer, but the position of the -COOH binding group varies the molecular orientation between 41° and 64° for the para- and meta-substituted sensitizer molecules. 115 When corrected for surface roughness, the angles obtained by p-ATR were in reasonable agreement with those from molecular dynamics simulations (Figure 12b), indicating that theory may provide a guiding path toward new, targeted assemblies. This result

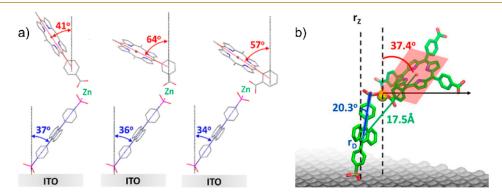


Figure 12. (a) Schematic depiction of the mean orientation of TTA-UC bilayers with respect to the position of the second layer binding group position. (b) Average structure for the para-COOH porphyrin from the MD simulations. Reproduced with permission from ref 115. Copyright 2020 American Chemical Society.

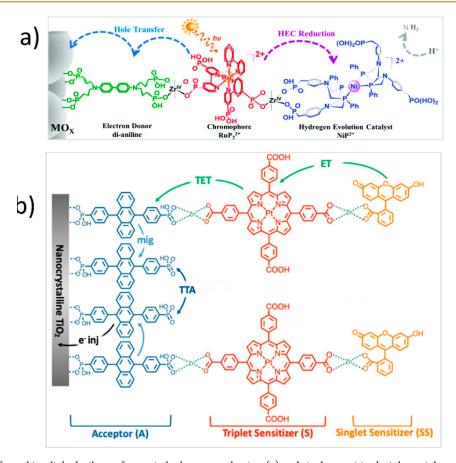


Figure 13. Examples of metal ion-linked trilayers for use in hydrogen production (a) and singlet sensitized triplet—triplet annihilation upconversion (b). (a) Reproduced with permission from ref 123. Copyright 2016 Royal Society of Chemistry. (b) Reproduced with permission from ref 128. Copyright 2019 American Chemical Society.

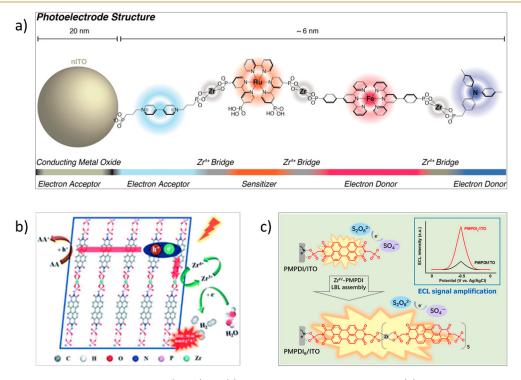


Figure 14. Examples of metal ion-linked multilayers (n > 3) for (a) long-lived charge separated states, (b) hydrogen generation catalysis, and (c) electrochemiluminescence sensing. (a) Reproduced with permission from ref 129. Copyright 2018 Wiley-VCH. (b) Reproduced with permission from ref 130. Copyright 2021 Royal Society of Chemistry. (c) Reproduced with permission from ref 132. Copyright 2022 Elsevier.

provided the first structural insights into the relative orientation of two independent species in a metal ion-linked multilayer.

3.3. Trilayers

Building upon the bilayer films, both figuratively and literally, there are several demonstrations of metal ion-linked trilayers on mesoporous metal oxides with select examples shown in Figure 13. The ability to include three independent molecular components enabled Farnum et al. to generate a MO_x -acceptor-chromophore-donor system that acted as a molecular p/n junction. Following photoexcitation, rapid interlayer electron transfer resulted in the formation of a charge separated state whose lifetime was >5 s. Aspects of electron transfer mediators, molecular p/n junctions, and photocatalysts were later combined to generate trilayers for use in H_2 generation and CO_2 reduction DSPECs (Figure 13a). CO_2 reduction DSPECs (Figure 13a). CO_2 reduction DSPECs (Figure 13a).

Trilayers have also been used to increase light absorption via the addition of a third chromophore. The most straightforward example is a trilayer composed of similar ruthenium(II) polypyridyl dyes for use in hydrogen generation photocatalysis. The trilayer has also been shown to be effective in increasing photocurrent generation in TTA-UC solar cells via the addition of a triplet and singlet sensitizer layer on top of the sensitizer-annihilator bilayer. The latter is particularly remarkable as the film undergoes excitation of the third layer, singlet energy transfer to the second, and triplet energy transfer to the first, followed by TTA and electron injection into the metal oxide as depicted in Figure 13b. The resulting 0.315 mA cm⁻² under 1 sun irradiation still stands as the record photocurrent generation from a TTA-UC solar cell and is enabled by the cooperative absorption of the singlet and triplet sensitizer layers. ¹⁰⁷

3.4. Beyond Trilayers

Extending beyond trilayers becomes challenging due to the fundamental limits as to how many layers can load within the pores of the mesoporous film. 84 Nonetheless, there are several assemblies containing four or more molecular layers with some examples shown in Figure 14.

In an extension of the bilayer and trilayer molecular rectifiers, a tetralayer system composed of a ${\rm MO_x}$ -sensitizer-chromophore-donor-donor was introduced to generate long-lived charge separated states (Figure 14a). Also similar to trilayer systems, the charge separation capabilities of these films is advantageous for hydrogen generation (Figure 14b), and water oxidation photocatalysis. The increased absorption for even homogeneous multilayers also makes them a promising scaffold for application in electrochromism and electroluminescent sensors for dopamine (Figure 14c). The latter report is notable in that they describe an eight-layer soaking procedure but observed that the absorption intensity (i.e., multilayer loading) was largely unchanged after six layers, suggesting they achieved the maximum multilayer thickness for their mesoporous film.

4. CONCLUSION

Here, we have recounted the more than 35-year journey of metal ion-linked multilayers and their transition from planar to mesoporous substrates and from homogeneous to heterogeneous multilayers. The ability to readily mix and match

components in a structured way, combined with the judicious choice of molecules based on their excited state energies and redox potentials, has enabled the directional control of energy and electron transfer events towards or away from an inorganic substrate. These tunable properties have opened the door to the use of metal ion-linked multilayers in a range of applications including QCM sensing, electrochromics, solar energy harvesting, molecular rectifiers, photocatalysis, and more. Nearly all of these applications rely on interlayer energy and electron transfer, which in turn is dependent on the structure of the multilayers. A combination of ATR-IR, XPS, ellipsometry, UV-vis spectroscopy, AFM, grazing-incidence small-angle scattering, second harmonic generation, solid-state NMR, and other techniques has provided definitive evidence of the layered nature of these films. Furthermore, using polarized ATR, we have just recently obtained our first glimpse at the relative orientation of molecules within the multilayers. However, there is still much to be learned about these metal ion-linked multilayers. Questions include the following:

- (1) What is the coordinative environment around the linking ions, and can the ions be used to control the structure of subsequent layers? In addition to potentially controlling structure via strategic ion selection, these metal ions may be useful as photoactive, electroactive, and magnetoactive components to the films.
- (2) How much dynamic mobility is there in the multilayers? As in, does the distance and orientation between the molecules change, and if so, on what time scales? One can envision increased mobility being advantageous when sampling geometric space enables moments of favorable electronic coupling. Alternatively, a strictly rigid system could be used to rigorously align magnetic moments for spin communication, for example.
- (3) What role does the local environment and loading condition play (i.e., solvent, metal oxide, counterions) in dictating the multilayer structure? Even for a fixed set of molecules and linking ions, it may be possible to obtain different structures and properties based on films treatment strategies. While this would significantly increase the number of variables that dictate structure, this would add additional tools for fine-tuning the structure.
- (4) Can multilayers be designed to enhance or suppress specific energy and electron transfer moments at will? With the appropriate selection of metal ions and molecules, it may be possible to completely suppress unwanted resonance energy transfer, for example, through orthogonal alignment of their transition moments.

Ultimately, a better understanding of what dictates the structure of these assemblies and how much they can be controlled will be a pivotal next step in realizing the full potential of metal ion-linked multilayers in applications ranging from solar energy conversion to sensing.

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Notes

The authors declare no competing financial interest.

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