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Abstract
Langmuir–Blodgett methods are perhaps the original approach for achieving controlled deposition of organic thin films. Molecules are first organized into a monolayer array on the surface of water before transfer as a monolayer onto solid supports. Molecular monolayers, multilayers, and multilayered heterostructures can be achieved. The capability of exercising such control over thin film assemblies has attracted materials chemists and physicists to develop Langmuir–Blodgett films for studies on organic conductors, magnets, non-linear optics, rectifiers, and intermolecular electron transfer. This article reviews objectives in each of these areas and selects some specific examples from the literature to highlight the state of the art, mostly from the point of view of the chemical systems that are studied. Mixed organic/inorganic hybrid films represent a new direction for Langmuir–Blodgett films in materials science, combining conventional inorganic solid-state phenomena with the properties of the organic networks, and recent examples, taken principally from the authors' work, are highlighted.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Langmuir–Blodgett (LB) film methods are perhaps the earliest example of what is now called 'supramolecular assembly', providing the opportunity to exercise molecular level control over the structure of organic thin films. In this method, a single layer of molecules is first organized on a liquid surface, usually water, before being transferred onto a solid support to form a thin film with the thickness of a constituent molecule. If the process is repeated, multiply layered films can be prepared. The layer of molecules on a liquid surface is termed a *Langmuir monolayer* and after transfer it is called a *Langmuir–Blodgett film*. LB films provide a level of control over the orientation and placement of molecules in monolayer and multilayer assemblies that are difficult to otherwise achieve. LB films have been explored for applications that include electronics, optics, microlithography, and chemical sensors, as well as biosensors or biochemical probes [1, 2].

The technique is named after Irving Langmuir and Katharine Blodgett, researchers at the General Electric Company in the first half of the twentieth century. Langmuir, awarded the Nobel Prize for Chemistry in 1932 for his studies of surface chemistry, used floating monolayers to learn about the nature of intermolecular forces. In the course of his studies, Langmuir developed several new techniques that are by and large still used today in the study of monomolecular films. Together with Langmuir, Katharine Blodgett refined the method of transferring the floating monolayer onto solid supports. In addition to treating many practical details of LB methods, publications and patents by Langmuir and Blodgett cover a number of potential applications including controlling the reflectivity of glass, a step gage for optically measuring the thickness of thin films, submicron mechanical filters, and biosensing. Although the methods are commonly named after Langmuir and Blodgett, numerous observations and experiments on floating organic films predate them, and enjoyable accounts of this history are available [2].

Modern studies of floating monolayers and LB films fall largely into two areas. The first area includes detailed fundamental studies of the physical nature and structure of Langmuir monolayers and LB films. The other involves applications that take advantage of the ability to prepare thin films with controlled thickness and composition. Much of the current work toward applications derives inspiration from the pioneering work of Hans Kuhn [3], who, in the 1960s, moved
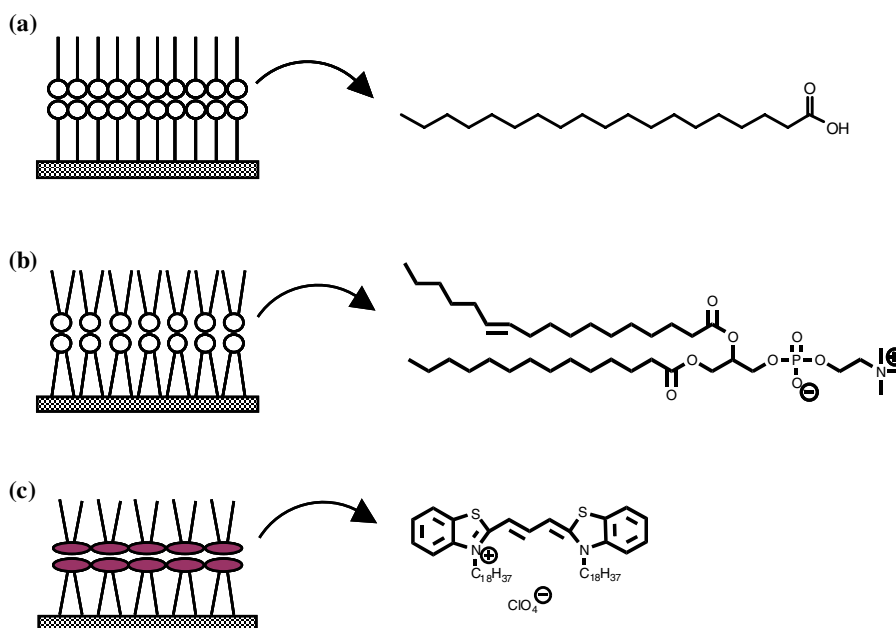
Figure 1. Traditional LB films composed of (a) a fatty acid (stearic acid), (b) a phospholipid (phosphatidyl choline) and (c) a cyanine dye (N, N'-dioctadecylthiacarbocyanine).

away from studies on fatty acids and other simple amphiphiles and used LB methods to control the position and orientation of functional molecules within complex assemblies (figure 1).

This review focuses on the use of LB film methods to produce organic thin film materials, highlighting examples of LB films for non-linear optics, photoinduced charge transport, unimolecular rectifiers, organic conductors, and magnetism. The article closes with recent examples of hybrid films that take advantage of the controlled deposition afforded by LB films to produce systems with mixed properties.

1.1. Langmuir monolayers

Essentially all LB film work begins with the Langmuir–Blodgett trough, or Langmuir film balance, containing an aqueous subphase (figure 2). Movable barriers that can skim the surface of the subphase permit control of the surface area available to the floating monolayer. To form a Langmuir monolayer, the molecule of interest is dissolved in a volatile organic solvent (frequently chloroform or hexane) that will not react with or dissolve into the subphase. Surface-active molecules are normally amphiphilic, with separate polar and hydrophobic groups, like the fatty acids studied by Langmuir and Blodgett [4]. A quantity of this solution is placed on the surface of the subphase, and as the solvent evaporates, the surfactant molecules spread. The movable barrier compresses the monolayer film, which will often experience different phases as a function of compression. Several techniques are available to monitor the state of the floating monolayer [1, 2].

As the pressure increases, the two-dimensional monolayer goes through different phases that have some analogy with the three-dimensional gas, liquid, and solid states. If the area/molecule is sufficiently high, then the floating film will be in a two-dimensional gas phase where the surfactant molecules are not interacting. As the monolayer is compressed, the
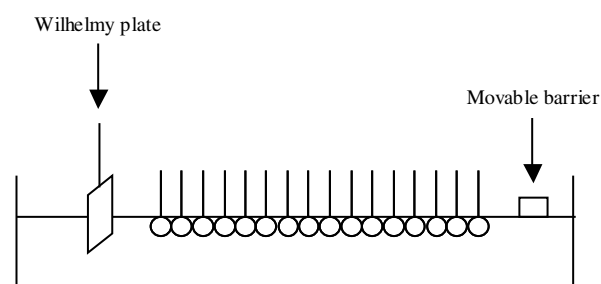

Figure 2. Langmuir monolayer on an LB trough. The Wilhelmy plate monitors surface pressure.

pressure rises signaling a change in phase to a two-dimensional liquid expanded (LE) state, which is analogous to a three-dimensional liquid. Upon further compression, the pressure begins to rise more steeply as the liquid expanded phase gives way to a condensed phase, or a series of condensed phases. This transition, analogous to a liquid–solid transition in three dimensions, does not always result in a true two-dimensional solid. Rather, condensed phases tend to have short-range structural coherence and are called liquid condensed (LC) phases. As the pressure is increased further, the monolayer will eventually collapse under the pressure, either sliding over upon itself, or folding under into the subphase.

1.2. Langmuir–Blodgett films

The term 'Langmuir–Blodgett film' traditionally refers to monolayers that have been vertically transferred off of the water subphase and onto a solid support such as glass, silicon, mica or quartz. Vertical deposition is the most common method of LB transfer; however, horizontal lifting of Langmuir monolayers onto solid supports, called Langmuir–Schaeffer deposition, is also possible [1, 2].
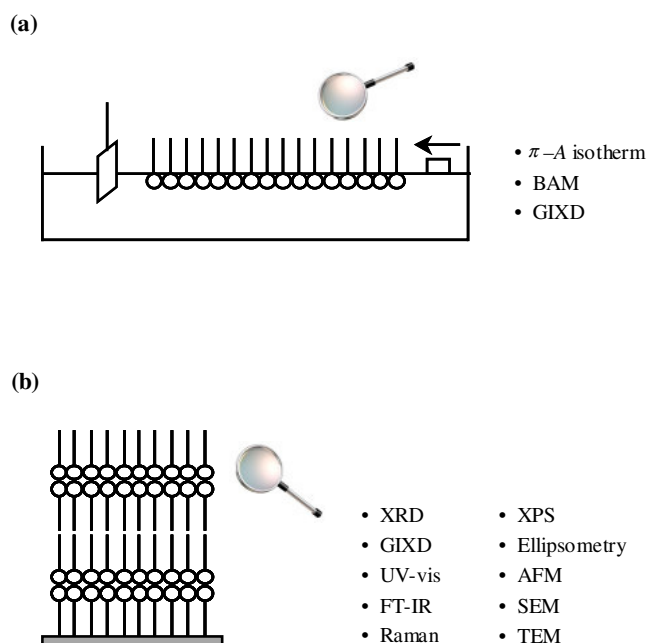
(a)　　　　　　　　　　　**(b)**

(i) Downstroke　　　　　　　(i) Downstroke

(ii) Upstroke　　　　　　　　(ii) Upstroke
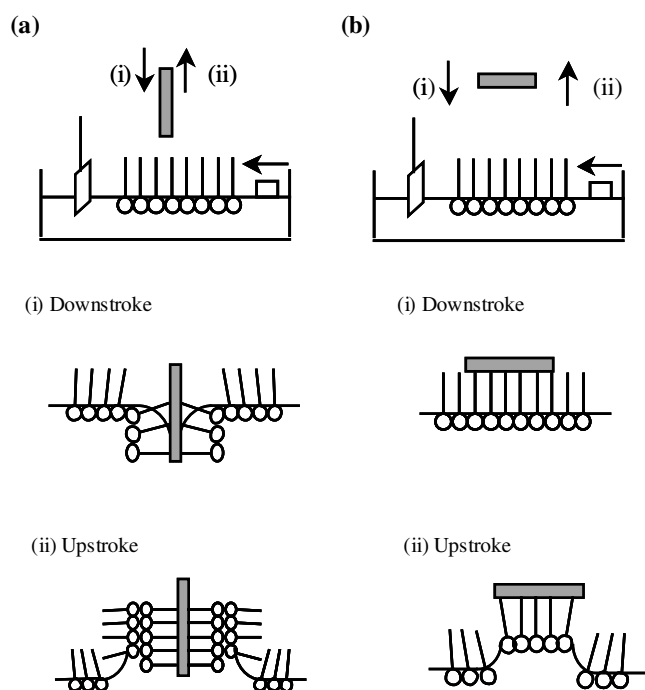
Figure 3. Deposition techniques starting with a hydrophobic substrate. (a) Vertical dipping method (Langmuir–Blodgett deposition) and (b) horizontal lifting method (Langmuir–Schaeffer deposition).

(a)

• π–A isotherm
• BAM
• GIXD

(b)

• XRD　　• XPS
• GIXD　• Ellipsometry
• UV-vis　• AFM
• FT-IR　• SEM
• Raman　• TEM

Figure 4. Methods used to characterize the molecular films. (a) At the air–water interface and (b) transferred films onto a solid support.

Either highly hydrophilic or highly hydrophobic substrates are desired. When hydrophobic, the substrate originates above the water surface. After the monolayer has been spread and compressed to the desired transfer pressure, the substrate is dipped vertically through the monolayer with transfer via the hydrophobic interactions between the alkyl chains and the surface. A hydrophilic substrate is submerged in the aqueous subphase prior to the spreading and compressing of the monolayer film. After the monolayer is stabilized, the substrate is withdrawn from the subphase, and the hydrophilic interactions drive the transfer (figure 3).

1.3. Characterization of LB films

Many analytical techniques are used to study transferred films (figure 4). In addition to the targeted materials properties, film characteristics that are typically of interest are thickness, interlayer spacing, molecular orientation and packing, film coverage, surface topology, and chemical composition [1, 2, 5, 6]. X-ray diffraction is a reliable technique to probe interlayer spacing, from which film thickness can be inferred. However, even x-ray diffraction is not proof that an LB film transfers layer by layer. Many amphiphiles, when condensed, will do so with a layered structure, which will look similar in x-ray diffraction as to well-organized LB film. Some measure of the uniformity of the film should complement x-ray diffraction. Film thickness can also be determined by ellipsometry or x-ray or neutron reflectivity. Transmission electron diffraction has also been observed from LB films and used to determine molecular packing, although the organic films are mostly unstable to

the electron beam. Atomic force microscopy (AFM) with molecular scale resolution has also been used to observe the arrangement of molecules in transferred monolayer and multilayer films [7].

To study the chemical make-up of the films, standard spectroscopic methods are used including FTIR, Raman scattering, and UV–visible absorption [8]. These methods are often sensitive enough to be applied to even monolayer films. Solid-state NMR has also been applied to LB films but is complicated by the small amount of materials available, so these studies are not routine [9]. The elemental composition can be determined with x-ray photoelectron spectroscopy (XPS) [10, 11]. However, the intensities of the XPS peaks are sensitive to many parameters such as an element's photoelectron escape depth and the film geometry, factors that complicate the determination of the elemental ratios.

2. LB Films as optical, electronic, and magnetic materials

LB films have been studied in conjunction with many different materials properties. Only a sampling are covered here, including films for non-linear optics, conductivity, magnetism, vectorial electron transfer, and unimolecular rectifiers. Within each topic, we have not attempted to be comprehensive, but rather choose a range of early and recent examples to illustrate important considerations and results for each topic. A newer focus of LB films is hybrid properties, mixing components chosen to contribute different phenomena that are combined in a single film. The article closes with some recent developments in hybrid films, chosen mostly from our own experiences.

2.1. Non-linear optics

The ability to prepare oriented arrangements of molecules make LB methods natural choices for organizing molecular chromophores for non-linear optics (NLO) applications, such as second harmonic generation (SHG), that require an asymmetric charge distribution along the primary molecular axis to extend to the condensed phase [12]. Organic NLO chromophores typically contain both donor and acceptor units connected via a π-bridge. The natural tendency for such molecules to condense in an antiparallel arrangement must be overcome to achieve SHG and other even ordered NLO effects in condensed phases. The LB technique enables the control of molecular architecture in such a way as to build non-centrosymmetric monolayers [12]. The trick, then, is to retain the asymmetry in transferred films by enforcing head-to-tail transfer or by including inactive spacer layers in traditional head-to-head followed by tail-to-tail transfers.

Hemicyanine dye derivatives are extensively studied as SHG chromophores and compound **1** provides a good illustration of the issues involved in generating SHG in LB films. The donor–π-bridge–acceptor chromophore provides the polar headgroup to which a hydrophobic group is added by alkylating the pyridyl nitrogen in **1** [12]. The molecule forms stable Langmuir monolayers that can be effectively transferred. In multilayer films, the molecule forms centrosymmetric head-to-head bilayers. However, if the deposition is alternated with passive spacer layers, non-centrosymmetric films are produced. A variety of spacers can be chosen, but compound **2** was shown to be particularly effective, designed to allow interlocking of the alkyl tails in multilayer films [12]. For the interleaved structure, the SHG intensity obtained from 200 layers, approximately 0.5 μm total thickness, is 18 300 times the signal from a monolayer of a comparable dye and shows the expected quadratic enhancement with film thickness. Many other parent NLO chromophores have been similarly studied in alternating layer LB films, including azobenzenes, stilbenes, coumarins, merocyanine dyes, and phthalocyanines [12–14].
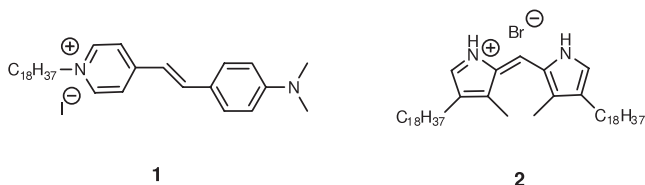
Alternating active and passive layers has generally been the most successful approach when it comes to generating non-centrosymmetric films for NLO. However, other strategies have also been employed. Complementary molecules, one with a hydrophobic tail attached to the donor and the other with a hydrophobic acceptor group can be alternately deposited to generate films with two active layers, each with their donor–acceptor dipoles in similar orientations [12]. Another way to generate the required asymmetric charge distribution is to use the LB method to create an interface between discrete donor and acceptor molecules. Bjørnholm and co-workers [15] illustrated the concept by alternating layers of an amphiphilic thiobenzoquinone acceptor, **3**, with an amphiphilic dioxadibenzoperylene donor, **4**. Second harmonic generation
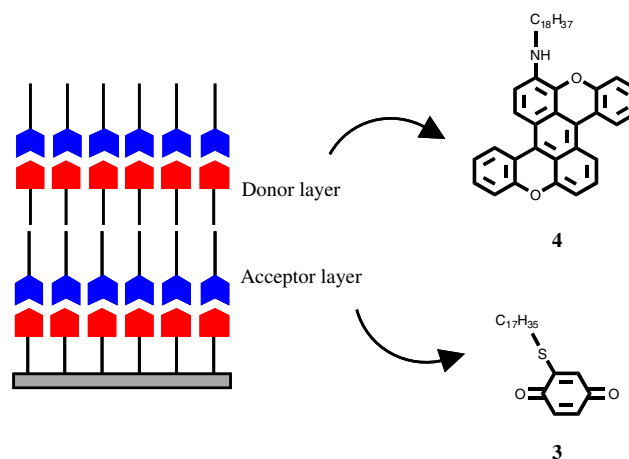
Figure 5. Donor–acceptor alternating LB films adapted from [15]. The acceptor molecule is an amphiphilic thiobenzoquinone, 3, and the donor molecule is an amphiphilic dioxadibenzoperylene, 4.

was observed and attributed to the hyperpolarizability resulting from intermolecular interactions between layers (figure 5).

Single component films have been achieved from molecules designed to deposit in a head-to-tail fashion. For example, zwitterionic dyes such as **5** form non-centrosymmetric multilayers driven by Coulombic interactions [16]. Alternatively, chromophores with hydrophobic groups appended to both donor and acceptor moieties, such as compound **6**, can apparently reorient during deposition to align with interlocking alkyl groups [17]. The interdigitation enhances stability and structural coherence of the film. Another strategy for controlling molecular orientation and controlling in-plane interactions is to build in structure-directing elements such as hydrogen bonding networks [18].
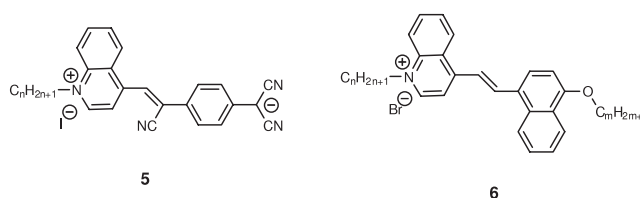
2.2. Directional electron transfer

The elaborate molecular machinery of the photosynthetic pathway continues to inspire efforts to artificially control the alignment and orientation of molecular components to achieve complex functions such as unidirectional electron transport. Langmuir–Blodgett deposition has been an important tool for preparing highly organized molecular assemblies in which intermolecular interactions such as distance, orientation, and extent of interaction can be controlled. In general, two different strategies have been employed to achieve vectorial electron transfer in LB films for applications that include photoinduced electron transfer and molecular rectifiers. The first approach takes advantage of the one-layer-at-a-time deposition process to position the various molecular components at different positions within a cooperative multilayer assembly. The
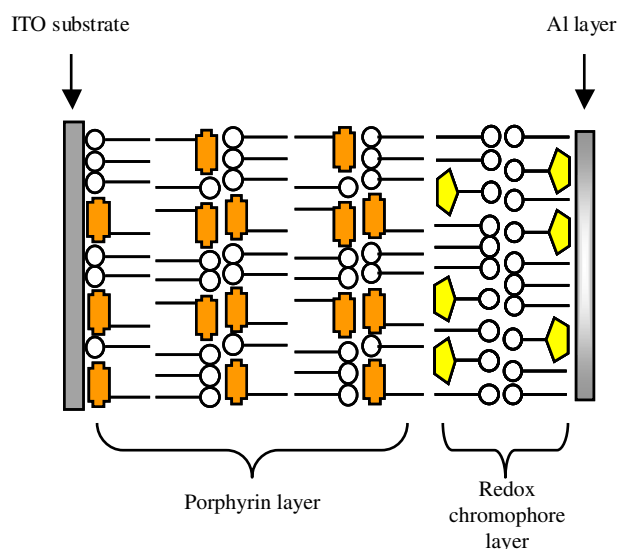
Figure 6. Photocarrier conductive LB films. The LB films are composed of amphiphilic porphyrin layers and charge transporting redox chromophore layers sandwiched between two electrodes. Adapted from [20].

second strategy is to use LB deposition to orient prefabricated molecular dyads or triads.

The potential of using monolayer techniques to organize molecular components for electron transfer and energy transfer was demonstrated by Kuhn and co-workers [3] working with long-chain substituted cyanine or azo dyes mixed into fatty acid monolayers. This early work illustrated how the orientation of the chromophore within the monolayers could be controlled by altering the alkyl substituents on the dyes and that the efficiency of energy transfer between photoexcited dyes and acceptors depends on their relative placement within multilayer assemblies. Such assemblies were also used to observe how the distance between the interfaces at which donor and acceptor chromophores were located influenced the efficiency of photoinduced electron transfer [19]. These concepts have led to the generation of photocurrents and to control of photocarrier conduction by incorporating redox chromophores into LB assemblies, as shown schematically in figure 6 [20].

In an A–S–D triad, an electron acceptor (A), a sensitizer (S), and an electron donor (D) are combined into a single molecule by σ-bonded bridges. Upon excitation of the sensitizer, a two-step electron transfer occurs, from S to A and from D to S, generating a charge separated state, $A^{\bullet-}$–S–$D^{\bullet+}$. The lifetimes of the excited states can be increased by controlling the alignment and orientation of the triad molecule, but as with NLO chromophores, the natural tendency for dipolar molecules to condense in an antiparallel arrangement must be overcome. Again, LB assemblies provide a natural tool for preparing oriented assemblies [21, 22].

The molecular triad **7** containing a pyrene sensitizer separating a viologen acceptor from a ferrocene donor provides a good example of the influence of LB alignment [21, 22]. With the aid of a fatty acid co-surfactant, LB films containing the oriented triad can be produced. Transient absorption

measurements of the molecule in solution estimate the lifetime of the photogenerated charge separated state as about 60 ns. On the other hand, extremely slow decay, approaching seconds, is observed in an LB film of the triad **7** codeposited in a matrix of fatty acid. The slow decay in the organized film is attributed to lateral charge migration between adjacent molecules in the monolayer planes facilitating charge separation [22]. A mixed strategy that combines a molecular ASD triad with separate light harvesting and electron donor molecules in a multilayer assembly also leads to long-lived charge separated states by mimicking the primary steps in natural photosynthesis [21].


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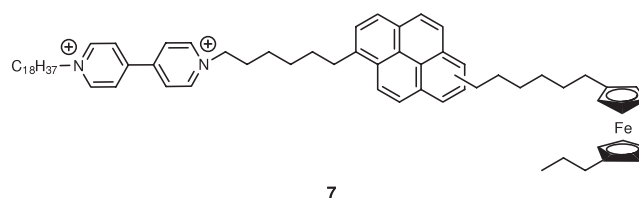
### 2.3. Unimolecular rectifiers [23]

The concept of a molecular rectifier was postulated more than 30 years ago. The Aviram and Ratner [24] proposal was that donor and acceptor units covalently linked by a poorly interacting bridge would preferentially pass charge in one direction. The proposed charge transport mechanism involves inelastic tunneling through the bridge converting an electronic excited state back to the ground state. The idea is that charge transport to and from respective electrodes to generate a $D^{\bullet+}$–b–$A^{\bullet-}$ excited state is far preferable to the reverse transport that would require generating the highly undesirable $D^{\bullet-}$–b–$A^{\bullet+}$, with b representing the covalent link between donor and acceptor parts of the molecule. The problem becomes how to demonstrate the phenomenon [23, 25]. A single molecule cannot be targeted, so an array of molecules needs to be immobilized for contact either by macroscopic sandwiching electrodes, or by using an STM tip and a conducting surface. In either case the, the molecules must be oriented on a surface. The task is a perfect one for a Langmuir–Blodgett monolayer, and many of the known examples of unimolecular rectifiers have been tested using LB methods.

The first confirmed example of unimolecular rectification used an LB film of molecule **8**, hexadecylquinolinium tricyanoquinodimethanide, sandwiched between metal electrodes [26, 27]. The bridge between donor and acceptor components is a π-system that is twisted, thus reducing delocalization. Rectification has been observed in both aligned multilayers as well as in monolayer films. As one might imagine, applying contacts without disrupting or shorting the molecular thin film can be problematic, and early efforts at measuring molecular rectifications were plagued by ambiguities. However, techniques for depositing contacts while preserving the molecular features within the thin films have been developed [23, 25, 28]. The mechanism of current rectification via **8** is thought to be a variation on that originally proposed by Aviram and Ratner. Molecule **8** is actually a zwitterion in its ground state and the first excited state is the form with neutral donor and acceptor moieties [23, 27]. The zwitterion form

favors head-to-tail orientation in multilayer films facilitating unidirectional electron flow.


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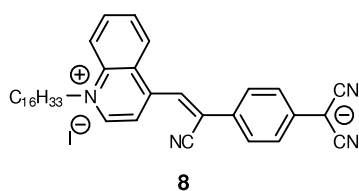
Many other D–b–A dyads have been prepared and investigated as molecular rectifiers, as detailed in recent reviews [23, 25]. The original suggestion of Aviram and Ratner [24] was for a TTF (**9**) donor bridged to a TCNQ (**10**) acceptor, coming on the heals of the then recent discovery of metallic behavior in the charge transfer salt TTF–TCNQ [29]. Recently, Bryce and co-workers reported the synthesis and LB film-forming behavior of the TTF–σ-TCNQ dyad, **11** [30], and electrical rectification was reported in an LB film of a related TTF-containing dyad, **12** [28]. An alternative acceptor to TCNQ is C_{60} and fullerene-containing dyads have been studied as rectifiers. Langmuir–Schaeffer films of molecule **13** [25, 31] placed between gold electrodes show electrical rectification. Finally, an alternative approach of depositing charged amphiphiles is exemplified by the D-π-A-π-D chevron-shaped dye, **14**, which transfers as an LB layer onto an oppositely charged SAM-modified gold support [32]. A rectification ratio of 25 at ± 1 V was measured using a PtIr STM probe.

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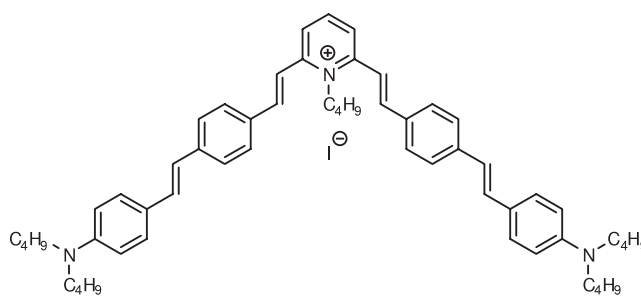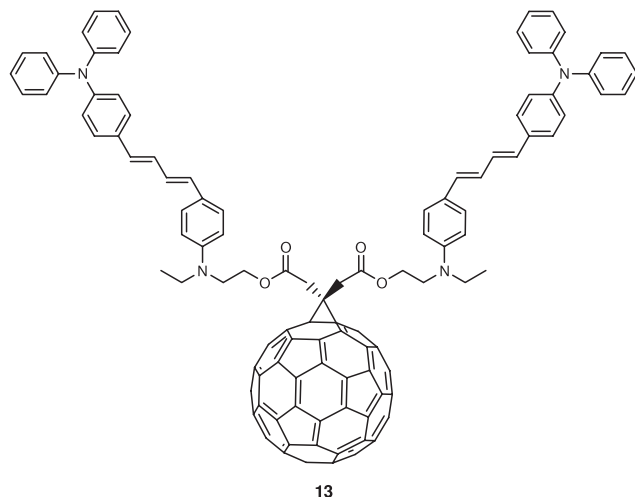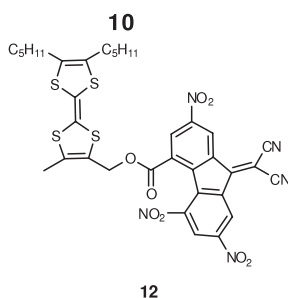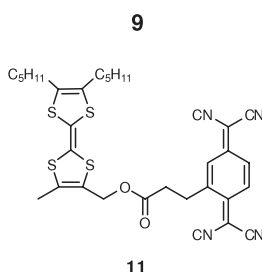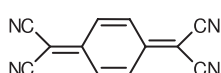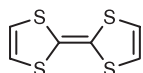
2.4. Organic conductors

Molecule-based conductors depend on intermolecular interactions and therefore the arrangement of molecules in condensed phases. Electronic band structures are determined by the distances between molecules and their orientation relative to each other. Despite significant advances in understanding the factors that dictate molecular packing, the ability to design a functional molecule and predict how it will arrange in the solid state is quite limited. The LB method provides at least some level of control over the orientation and placement of molecules in monolayer and multilayer assemblies [8, 33–37].

Routes to form conducting LB films generally involve molecular building blocks similar to those used in the pursuit of conducting molecular solids, principally TTF family donors, TCNQ family acceptors, metal dithiolate complexes, and phthalocyanines. To form monolayers at the air/water interface, the basis molecules must be included in an amphiphilic assembly. One approach is to substitute the basis molecule to make it amphiphilic, by adding hydrophobic groups, as in the substituted TTF's **15** and **16** [38], or by substituting with both hydrophobic and hydrophilic groups, as in the TTF derivative, **17** [39]. Another approach, sometimes called the 'semiamphiphilic approach [8], is to associate the non-amphiphilic active molecule with an amphiphilic counterion, as for the pyridinium TCNQ salt, *N*-docosylpyridinium–TCNQ (**18**) [40, 41].

15: X = O
16: X = S

17

18
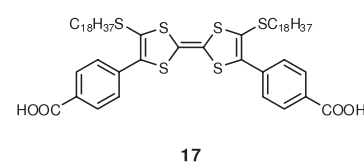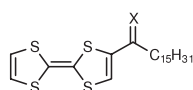
The resulting films are often comprised of either neutral or fully charge transferred basis molecules and subsequent treatment to achieve mixed valency can be required to form conducting films. The most common route to doped films is post-deposition chemical treatment, for example with a vapor phase oxidant such as I_2 [38, 41]. While oxidation is normally achieved, films are sometimes unstable to back charge transfer

and outgassing of the dopant. Another way to achieve mixed valency is to start with a mixture of neutral and charged basis molecules to give an average oxidation state in the final assembly [42]. Alternatively, the film can be a traditional charge transfer salt, comprised of donors and acceptors, one or both of which have been substituted to be amphiphilic [43].

Raudel-Teixier, Vandevyver, and Barraud prepared the first examples of conductive LB films using **18** [44]. Upon LB film transfer, the TCNQ is anionic, so subsequent oxidation with iodine vapor was used to achieve mixed valency. These authors, along with Nakamura and co-workers, mapped out the use of a combination of analytical methods to learn about the structure of the conducting LB films [40, 41, 44, 45] and determined that in the precursor film (TCNQ$^-$)$_2$ dimers are oriented with their molecular planes parallel to the substrate surface, but upon partial oxidation, the TCNQ moieties reorient to align the long molecular axis perpendicular to the substrate. The conductivity after treatment was 0.1 S cm^{-1} with an activation energy of 0.15 eV. However, the film has a domain structure, with less organized grain boundaries separating the more highly conducting domains. Therefore, the measured conductivity is less than the intrinsic conductivity, estimated to be as high as 200 S cm^{-1} from optical measurements. This feature of the macroscopic conductivity being limited by domain structure and film imperfections has turned out to be a common feature of conducting LB films [35, 36].

The amphiphilic TTF derivatives HDTTF (**15**) and HDTTTF (**16**) illustrate the idea of modifying a TTF donor to generate film-forming amphiphiles [34, 38, 46]. The neutral amphiphiles spread on water and can be deposited onto a variety of substrates films using normal dipping procedures. Chemical oxidation after deposition is required to form a charge transfer salt, and iodine vapor oxidation has been the most successful approach. Initial exposure to iodine generates fully oxidized TTF cations, but the film gradually releases iodine to stabilize in a mixed-valence conducting state. The films also reorganize after doping with interdigitation of the alkyl groups on adjacent layers. IR and optical measurements suggest a nearly vertical orientation of the amphiphile after doping with respect to the solid support surface. The conductivity of the oxidized thiocarboxy analog is the highest in the series. The two-probe dc conductivity was measured as 1.0 ± 0.2 S cm^{-1} with activation energy of 0.09 eV. This conductivity is high for an LB film, but low compared to related solid-state charge transfer salts.

Metallic LB films were fabricated from the donor BEDO–TTF (**19**) that forms semiamphiphilic monolayers as the cation–radical salt of behenate or stearate amphiphiles [37, 47, 48]. The preparation is one of the simplest for a conducting LB film, and at the same time, represents the most clear-cut example of a conducting molecule-based LB film. The donor and the fatty acid are spread together from chloroform at the air/water interface [47]. Partial oxidation of BEDO–TTF occurs spontaneously, and the donors associate with the carboxylate ions that are confined to the air/water interface. There is speculation that the oxidation is proton assisted, but the exact mechanism of cation–radical formation is still unclear. Nevertheless, this assembly can be transferred by

normal vertical dipping procedures to obtain multilayered LB films.
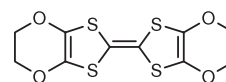
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Macroscopic dc conductivity up to 100 S cm^{-1} has been measured, and the temperature dependence of the conductivity is that of a metal to below 150 K. Infrared reflection–absorption spectroscopy at the air/water interface indicates that the monolayer assembly is already conducting [47]. A broad electronic absorption band in the IR can be treated with the Drude model to yield an optical conductivity $\sigma_{opt} \sim 200$ S cm^{-1} for the monolayer. Upon transfer, multilayers assume a bilayer structure, and a model for the structure, consistent with x-ray diffraction, EPR data, and IR spectroscopy consists of BEDO–TTF bilayers organized in a sheet, sandwiched between two layers of fatty acid.

Phthalocyanines have long been studied in LB films [1, 2, 35, 49, 50]. Symmetric, non-amphiphilic derivatives are known to form Langmuir monolayers of face-to-face stacked macrocycles in columns parallel to the water surface [2]. Recent efforts have sought to improve film processing and electronic characteristics through a series of octasubstituted phthalocyanines, such as **20** [51–54]. At the air/water interface, the face-to-face stacked phthalocyanines reorganize upon compression, stabilizing as apparent bilayers. These films can be transferred to hydrophobic supports, using either vertical or horizontal dipping methods, to yield continuous films corresponding to a bilayer thickness of columns of the stacked phthalocyanines. The direction of the columns can be influenced by the barrier motion so that the deposited films are highly anisotropic, with columns oriented parallel to the substrate, but also with a preferred in-plane direction. This is an important characteristic for any application that will take advantage of the anisotropic nature of the assemblies. Conductivities of the phthalocyanine films in the range 10^{-9}–10^{-8} S cm^{-1} are observed that increase 2 or 3 orders of magnitude upon electrochemical doping. Before and after doping, the conductivity along the column direction is significantly larger than perpendicular to it, with anisotropy approaching 1000 to 1 [54].
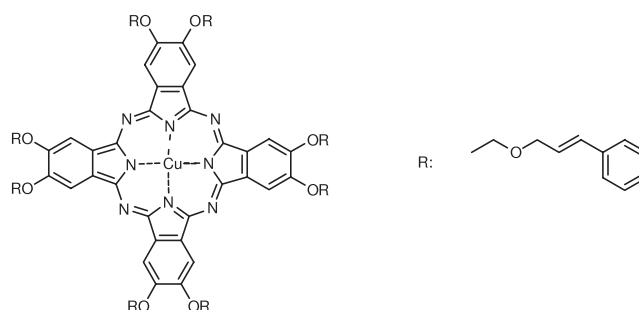

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2.5. Magnetism

Unlike the properties discussed so far, NLO, electron transfer, and conductivity, for which the thin film behavior derives from
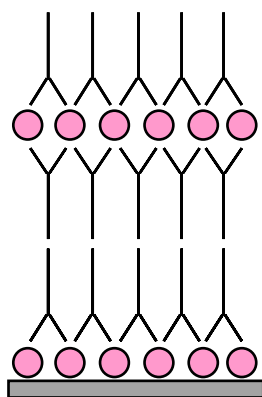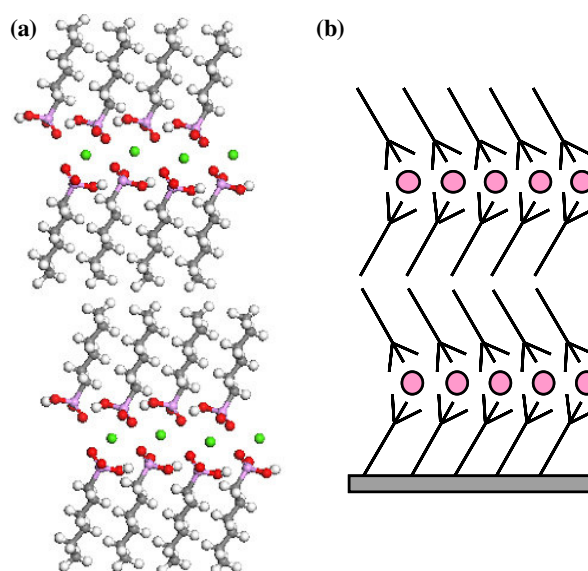
Figure 7. Manganese stearate LB films. Circles represent the Mn^{2+} ions arranged into a 'literally two-dimensional' sheet [58].

Figure 8. (a) Layered structure of metal alkylphosphonate exemplified by $Ca(O_3PC_6H_{13})_2$ from the crystal structure adapted from [67]. (b) Scheme illustrating of structure of manganese–phosphonate LB films composed of octadecylphosphonic acid, 22, and manganese ions. Circles represent the Mn^{2+} ion.

the organic molecular constituents, most studies of magnetism in LB films have involved assemblies of inorganic ions or molecular complexes [33]. The relatively few examples of organic-based magnetism in LB films center on amphiphilic nitronyl–nitroxide radicals such as the radical, **21**, synthesized by Le Moigne *et al* [55]. Magnetic studies [56] on an LB monolayer were compared to the same molecule in a cast film. SQUID magnetometry reveals weak antiferromagnetic interactions in the cast film, with a Weiss constant of $\theta = -0.9$ K. In contrast, a monolayer deposited onto silica displays ferromagnetic interactions in EPR measurements. The temperature dependence of the magnetic susceptibility, derived from the EPR intensity, yields a positive Weiss constant, $\theta = 2.5$ K, indicating ferromagnetic interactions. The result shows that the Langmuir–Blodgett technique effects control over intermolecular magnetic interactions. The molecular organization in the monolayer, where the headgroup interacts with the silica substrate, provides for different exchange pathways than are present in the cast film.


21
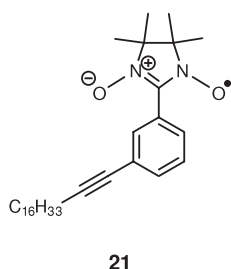
Far more work has involved films of metal ions or complexes organized into two dimensions by the organic monolayers. The earliest extensive investigation of magnetism in LB films was conducted by Pomerantz and co-workers working at the IBM T J Watson Research Center in the late 1970s [57–59]. These authors used careful EPR measurements to demonstrate antiferromagnetic exchange within a monolayer of manganese stearate and provided evidence for a magnetically ordered state at low temperature. The Mn^{2+} ions were confined to a single layer between two stearate layers deposited head-to-head using traditional vertical dipping (figure 7). Evidence for magnetic exchange in two dimensions was demonstrated using EPR on a stacked

sample of 50 slides, each containing a manganese stearate bilayer. The authors concluded that the manganese stearate monolayers order in a canted antiferromagnetic state. Other groups have independently observed magnetic ordering in manganese [60, 61].

Metal phosphonates have provided somewhat clearer examples of magnetic LB films. For example, octadecylphosphonic acid, **22**, forms LB films with a variety of divalent, trivalent or tetravalent metal ions resulting in layers of the metal ions sandwiched within bilayers of the organophosphonate [62–66]. What is significantly different from the metal carboxylate films is that solid-state metal phosphonates form layered continuous lattice structures [67], so that it has been possible to learn details about the in-plane structure of the LB films by comparing them to the known solids (figure 8).

$$C_{18}H_{37}\text{—}PO_3H_2$$

22
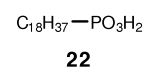
The most extensive magnetic studies have been on manganese phosphonate LB films [63, 68–73]. In the solid state, manganese alkylphosphonates are layered solids, with sheets of manganese ions, in a distorted square array, bonded on top and bottom by layers of the organophosphonate (figure 8). Magnetic exchange within the layers is antiferromagnetic, and the solid-state alkylphosphonates $(C_nH_{2n+1}PO_3)Mn \cdot H_2O$ ($n = 2$–6) each order antiferromagnetically between 13 and 15 K [74, 75]. A weak moment develops below the ordering temperature and the solid-state phosphonates are known to be canted antiferromagnets [63, 73–75]. Manganese octadecylphosphonate LB films have been shown to have the same in-plane structure as the related solid-state compounds [63, 76], and like the solids, the films exhibit antiferromagnetic interactions. A magnetic ordering transition is

(a)　　　　　　　　　**(b)**
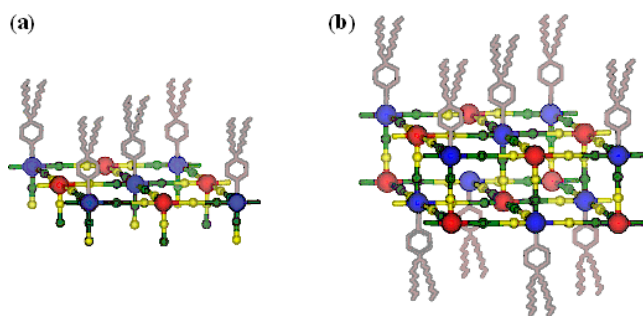
Figure 9. (a) A mixed metal cyanide bridged square-grid network at the air/water interface. Reaction of a Langmuir monolayer of the amphiphilic pentacyanoferrate (3+), 23, with aqueous Ni^{2+}, Co^{2+}, or Mn^{2+} ions from the subphase results in two-dimensional networks. Each metal ion is bridged by a cyanide ligand. (b) Bilayered films are formed after transferring two-dimensional networks by the LB technique.

observed in static magnetization measurements near 13 K [63]. The ordered state of the LB film is also a canted antiferromagnet and the films exhibit magnetic memory below T_N. Hysteresis is observed in the vicinity of zero field for positive and negative scans of the applied field as it is cycled between ± 5 T.

Magnetic films have also been prepared from molecular complexes, assembled into a two-dimensional extended network on an LB trough. Reaction of a Langmuir monolayer of the amphiphilic pentacyanoferrate (3+), **23**, with Ni^{2+}, Co^{2+}, or Mn^{2+} ions from the subphase results in two-dimensional mixed metal cyanide bridged networks at the air/water interface (figure 9) [77–80]. Confinement of the reactants to the air/water interface discriminates against the formation of higher dimensionality products and directs the lateral propagation of the two-dimensional network. The networks can be transferred to various supports to form monolayer or multilayer lamellar films by the LB technique. The structure of the networks was confirmed with grazing incidence synchrotron x-ray diffraction (GIXD), which revealed a face-centered square-grid structure for each example with cell edges in the range of 10.2–10.4 Å, as expected on the basis of the related two- and three-dimensional solid-state analogs.

23
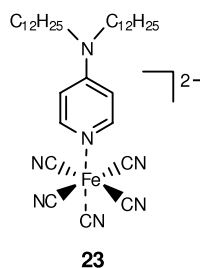
Metal cyanide extended networks, two-dimensional analogs of Prussian blue, are of interest to the molecule-based magnetism community [81, 82] because the nature of the magnetic exchange can be anticipated in advance from basic orbital interaction arguments and the predictable structure-directing quality of the cyanide bridge [83]. Magnetic susceptibility measurements on multilayered samples indicate that the Fe–Ni network undergoes a transition to a

ferromagnetic state below $T_C = 5.4$ K [77, 79, 84]. The ordering temperature of the LB film is lower than the $T_C = 23$ K observed in the three-dimensional cubic analog, but is similar to the ordering temperature reported in other low dimensional Fe–CN–Ni networks. [85]. Networks formed from **23** with Mn^{2+} of Co^{2+} are also magnetic at low temperature [78].

LB films of Prussian blue related compounds were also prepared by Mingotaud and co-workers [86, 87] by spreading a positively charged lipid such as dioctadecyldimethylammonium ion (DODA), **24**, on a very dilute colloidal dispersion of 'soluble' Prussian blue, $Fe_4[Fe(CN)_6]_3 \cdot 12H_2O$ [86, 87], or the mixed metal analog, $Cu_3[Fe(CN)_6]_2 \cdot 2H_2O$ [88]. The monolayers can be transferred forming Y-type films with the inorganic metal cyanide species trapped within the amphiphilic bilayer. The exact state of the metal cyanide species is very sensitive to the deposition conditions [89]. Higher subphase concentrations lead to 'rough' films, indicating that colloidal particles are transferred. However, at very low concentrations molecular species that are present in the subphase as a result of the dissociation of the colloidal particles appear to reassemble into a lamellar network [89].
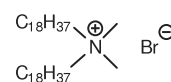

24

A ferromagnetic ground state is observed for both the Fe^{2+}/Fe^{3+} and the Cu^{2+}/Fe^{3+} mixed metal films. The Curie temperature for the Fe^{2+}/Fe^{3+} film is assigned as $T_C = 5.7 \pm 0.1$ K, which is slightly higher than that determined under the same experimental conditions for the commercial Prussian blue powder used as the precursor ($T_C = 5.1 \pm 0.1$ K) [87, 90]. The higher ordering temperature may be due to changes in structure, or could be a result of the anisotropic nature of the thin film. Strong anisotropy in the EPR line position (*g* factor) and the linewidth (ΔH in gauss) near T_C are consistent with a two-dimensional magnetic system.

3. Films with mixed properties

The layer-by-layer deposition process and the amphiphilic nature of the basis molecules make LB films ideal platforms for combining more than one targeted property into a single material. The film-forming molecules can be changed from one layer to the next to give superstructures in which the chemically different layers contribute different physical properties. Alternatively, the segregated hydrophobic and hydrophilic character of LB films can lead to mixed organic/inorganic films, or 'dual-network' assemblies, where the organic and inorganic components contribute separate properties [90, 91]. An example is a film that is both conducting and magnetic. Films with photoactive or electroactive components designed to switch the property of interest with external stimulus have also been targeted. A few recent examples illustrate the ideas.

3.1. Conducting and magnetic films

Mixed organic/inorganic 'dual-network' LB films have been prepared based on the organic donors **25** and **26** in which the polar network of the transferred films contain the magnetic manganese phosphonate lattice and the organic network contains the substituted TTF moiety [70, 71]. LB deposition of **25**, from an aqueous Mn^{2+} subphase forms Y-type films with stoichiometry $Mn_2(\mathbf{25})(H_2O)_2$. Since the donor has two alkylphosphonate arms, the film stoichiometry is consistent with the $Mn(O_3PR)H_2O$ structure known in other manganese phosphonate LB films and layered solids. The film becomes magnetic near 11.5 K when the manganese phosphonate network orders as a canted antiferromagnet, proving that the inorganic network has formed. The manganese phosphonate LB film based on **25** is also magnetic. Attempts to subsequently oxidize the TTF network of **25** did not result in stable phases. On the other hand, a manganese phosphonate LB film of the donor **26** [92] does form a stable phase when photooxidized in the presence of CCl_4 to form a chloride salt following the procedures described by Scott *et al* [93]. Optical spectroscopy indicates the doped organic network is semiconducting. Unfortunately, contact probe conductivity measurements yield high resistivity. AFM images showed the film was made up of distinct domains approximately 100 nm across that do not percolate over macroscopic distances. Even though spectroscopic evidence suggests the organic network is conducting, the film topography does not support charge transport.


25   **26**
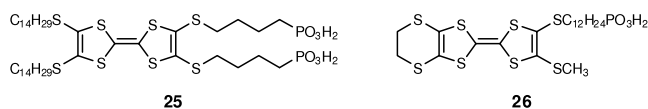
Another hybrid film was formed by alternating layers of magnetic polyoxometallate clusters with an organic donor molecule [94]. The cluster $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ was first transferred with a monolayer of the cationic surfactant DODA. A monolayer of the semi-fluorinated donor, **27**, was then transferred onto the hydrophobic surface provided by the DODA layer. Repeating the process generates multilayered films. Iodine vapor treatment oxidizes the donor leading to an electronic absorption in the IR consistent with charge delocalization. However, as for the previous example, the macroscopic conductivity did not increase after oxidation, suggesting that the structure of the film did not permit long-range delocalization.


27
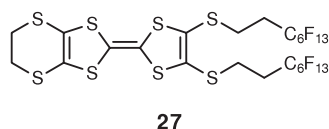
3.2. Photoswitching of magnetic properties

The heterostructured character of hybrid LB films provides opportunity to explore the photochemical switching of magnetic behavior by coupling a photoactive chromophore with a magnetic lattice. Some examples based on azobenzene chromophores have been attempted. For example, manganese

phosphonate LB films of the chromophore **28** have been prepared [95]. Spectroscopic analysis and GIXD confirm that the same extended lattice inorganic network observed for the octadecylphosphonate LB films forms even in the presence of the azobenzene group [76, 95]. The film orders magnetically, becoming a canted antiferromagnet below 14 K, providing further proof that the inorganic network forms. Unfortunately, in this system, *trans*-to-*cis* isomerization of the azobenzene is not effected upon UV irradiation. The close packing of the azobenzene chromophores in the mixed organic/inorganic film does not provide the flexibility and free volume needed for the isomerization to occur. As a result, there is no change in magnetic response with illumination.


28
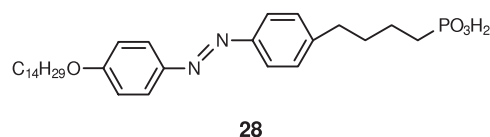
In another approach, the azobenzene chromophore is coupled with Prussian blue layers to switch the Prussian blue magnetism with light. The amphiphilic azobenzene, **29**, forms a hybrid monolayer with clay platelets adsorbed from the subphase [96]. After horizontal transfer, Prussian blue can be grown at the clay surface by alternately dipping the film in aqueous $FeCl_2$ and aqueous $K_3[Fe(CN)_6]$ solutions (figure 10). The process can be repeated to form multilayered films. Illumination of the hybrid films with UV light at 2 K to induce *trans*-to-*cis* isomerization decreases the magnetization by as much as 11%. The magnetization can be recovered upon *cis*-to-*trans* isomerization with visible light and the cycle can be repeated many times. The photoswitching of the magnetization is attributed to changes in the electrostatic field associated with reorganizing the film upon photoisomerization of the azobenzene. The clay platelet layer can be replaced with a polyelectrolyte, such as deoxyribonucleic acid, and the photomagnetic switching is still observed [97].

29
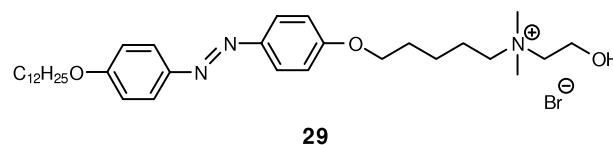
In the above examples, photoswitching of one component of the hybrid film induces a magnetization change in another component. However, hybrid LB films in which the inorganic component itself is photoswitchable have also been prepared. Photoinduced magnetism in the cobalt iron Prussian blue analogs, $A_jCo_k[Fe(CN)_6]_l \cdot nH_2O$, was discovered by Hashimoto and co-workers in 1996 [98], and subsequently studied by several groups [99, 100]. At temperatures below 20 K, diamagnetic $Fe^{2+}-Co^{3+}$ (ls) pairs may be photoexcited to a long-lived metastable ferrimagnetic $Fe^{3+}-Co^{2+}$ (hs) state through a charge transfer and spin crossover event increasing magnetization.

As discussed above, an $Fe^{3+}-Co^{2+}$ monolayer network prepared from the cyanoferrate amphiphile, **23**, using the procedures described in figure 9 produced a magnetic LB film. However, these films did not respond to UV–vis light. On the other hand, the metal cyanide Langmuir–Blodgett monolayers
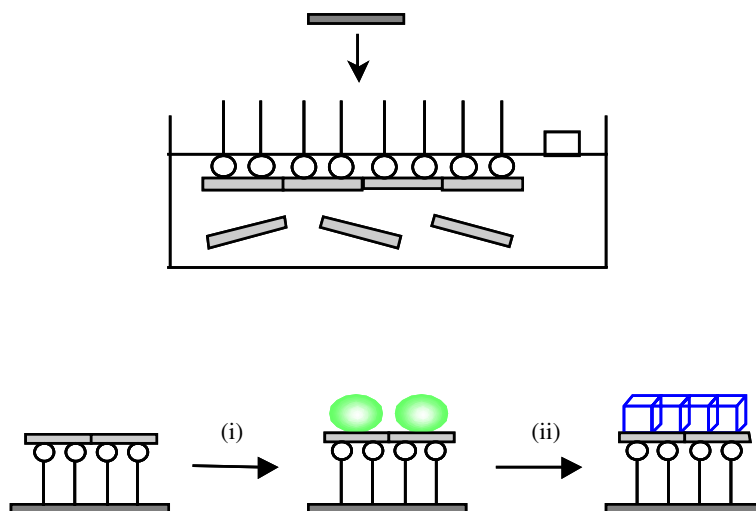
Figure 10. A modified LB method using a smectite clay mineral. Reaction of a Langmuir monolayer of a cationic amphiphile with negatively charged clay platelets from the subphase results in organic/inorganic hybrid monolayers at the air/water interface. After transfer the monolayer by the horizontal lifting method, the film is dipped in aqueous MCl_2 (step i) and $K_3[Fe(CN)_6]$ (step ii) solutions leading to the formation of Prussian blue layer. The process can be repeated to fabricate multilayered films.

could be used to template thin films of the bulk Prussian blue analog grown using a layer-by-layer deposition of Co^{2+} and $[Fe(CN)_6]^{3-}$ [80, 101]. Investigation of the magnetic and photomagnetic properties of the $A_jCo_k[Fe(CN)_6]_l \cdot nH_2O$ films prepared in this way showed that in addition to the magnetic and photomagnetic phenomena present in powdered solids, the thin films exhibit a new phenomenon, a photoinduced decrease in magnetization for a specific orientation of the film in the applied magnetic field [102–104]. The photomagnetic response of the thin films is anisotropic, increasing in one orientation and decreasing in the other. The behavior is explained with a model that depends on the quasi-two-dimensional structure of the films and the influence of residual magnetic moments in the film before photoexcitation.

Thin films of cobalt–iron cyanide Prussian blue analog were also fabricated by means of the modified Langmuir–Blodgett method (figure 10) using a smectite clay mineral, montmorillonite [105–107]. In this combined method, the clay LB films template the formation of the Co–Fe Prussian Blue thin layer. Structural analysis suggests a well-organized film not only with respect to the layered superstructure, for which a single metal cyanide layer is indicated, but also in the in-plane direction. In this system, photoinduced electron transfer from the iron ion to the cobalt through the bridging cyanide occurs at low temperature (8 K), similar to that observed in the bulk Co–Fe Prussian blue. The films exhibit magnetic anisotropy with respect to the direction of the applied magnetic field and the photoinduced magnetization in the films is also anisotropic [106, 107].

4. Summary

Langmuir–Blodgett film methods continue to provide routes to unique organic thin film materials. The key to LB techniques is the ability to control the organization of molecular components

on a molecular level. LB methods remain unparalleled with respect to the ability to spatially and orientationally organize different molecules in separate layers of molecular dimensions. Studies on non-linear optics, directional electron transfer, and molecular rectification take advantage of this capability. It is more difficult to precisely direct intermolecular interactions within layers, although LB methods do afford some level of control. Materials properties that depend on intralayer molecular packing include conductivity and molecule-based magnetism. The need to work with surface-active molecules on water, while on one hand providing the tool to control molecules, also limits the kind of intermolecular interactions that can be achieved. A very promising strength of LB methods is the opportunity to fabricate hybrid assemblies. Recent developments not only combine different organic components, but now permit formation of inorganic networks within LB assemblies. Exciting possibilities exist for combining organic molecule-based properties with cooperative solid-state phenomena in thin films and tuning interactions between the different networks at the molecular level.

Acknowledgments

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