

# Layer-by-Layer Electrostatic Self-assembly Method: A Facile Approach of Preparing Nanoscale Molecular Thin Films

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## Abstract

*Fabrication of thin films incorporating the nanosized objects is one of the important issues in modern nanoscience and nanotechnology. Various methods have been attempted to prepare nanoscale molecular thin films among which layer-by-layer electrostatic self-assembly method has become a prime choice in this direction. Over the last 15 years, the layer-by-layer (LbL) electrostatic self-assembly (ESA) technology has proven to be a versatile method for surface modification. This approach is likely to find widespread application because of its simplicity and versatility. This is a low cost and facile approach for assembling various organic and inorganic and bio materials onto solid substrate with diverse properties when compared to their solution or bulk crystalline phase. This technique relies on the electrostatic interactions between the oppositely charged species from their aqueous solution and in solid substrate. No complicated instrument is required in this method. LbL ESA method is an elegant choice for preparing thin films of functional dye molecules. Layer-by-layer (LbL) self-assembly has emerged as a versatile, gentle and, simple method for immobilization of various biomaterials in an easily controllable thin film morphology onto solid substrate. Recently organic-inorganic nanostructured thin films for various technological applications have been prepared by this method.*

**Key words :** Layer-by-layer, thin films, electrostatic self-assembly, adsorption, immobilization, organic-inorganic hybrid.

## 1. Introduction

Nanoscale molecular thin films with specific structures and properties have attracted much attention in recent years because of their numerous potential applications in diverse fields [1]. These well ordered films consisting of molecules with significant physical and physicochemical properties are carefully aligned between individual layers and substrates, processing high stability to thermal change and chemical environments.

A number of self-assembly techniques have been employed for film fabrication, such as Langmuir-Blodgett (LB) and covalently self assembled monolayer techniques. However these two methods for film fabrication require sophisticated and precise experimental conditions and limited

compatibility with diverse category of materials. In this purpose a new facile approach namely Layer-by-layer electrostatic self-assembly originally developed by Decher and co-workers [2] for preparing nanometer level molecular architectures using electrostatic adsorption between oppositely charged species onto solid substrate. In recent times this has led to intense interest in the development of the methods that can be used to engineer many important surface properties in a nanometer level. The alternate adsorption of polyanionic and polycationic molecules on oppositely charged surfaces is accomplished by immersion in aqueous polyelectrolyte solutions. This unique cost-effective method has many advantages including the ease of fabrications, the availability of various water soluble polyions and capability of uniform and stable multilayer synthesis. A wide variety of materials,

including functional materials, dyes, conducting polymers, layered silicate, metal and their oxide nanoparticles and many others [3-7]. This method allows for incorporating various building blocks into multilayered systems in a designed way.

This short review focuses the general overview and recent developments of layer-by-layer electrostatic self-assembly method for preparing nanoscale molecular thin films incorporating different organic, inorganic and biological materials with interesting physical and physicochemical aspects.

## 2. The LBL Electrostatic Self-assembly Method

The concept of the alternate adsorption of oppositely charged polyions began with Illers [8] demonstration of sequential deposition of negatively charged silica colloids and positive alumina fibrils in 1996. But this novel process was largely developed until the early 1990's, when Decher and coworkers

[9], at Gutenberg University in Germany, fabricated optically transparent multilayer films of four different polyelectrolytes [10]. Uniform growth can be verified using UV-Vis absorption spectroscopy and small angle x-ray scattering (SAXS). Figure 1 shows the schematic representation for a clear understanding of the LBL ESA method for film fabrication. In this method, a suitable substrate (quartz, glass, silica etc.) first dissolved in the aqueous solution of positively charge species (may be some poly-electrolytic solution). Then after rinsing with the ultra pure water following drying, the substrate is immersed in the solution of negatively charged molecules. After sufficient time to allow the adsorption of molecules the substrates is rinsed and dried under vacuum. In this way one bilayer LBL film can be deposited into the substrate. This process can be sequentially and alternately repeated to get the desired multilayered structures.

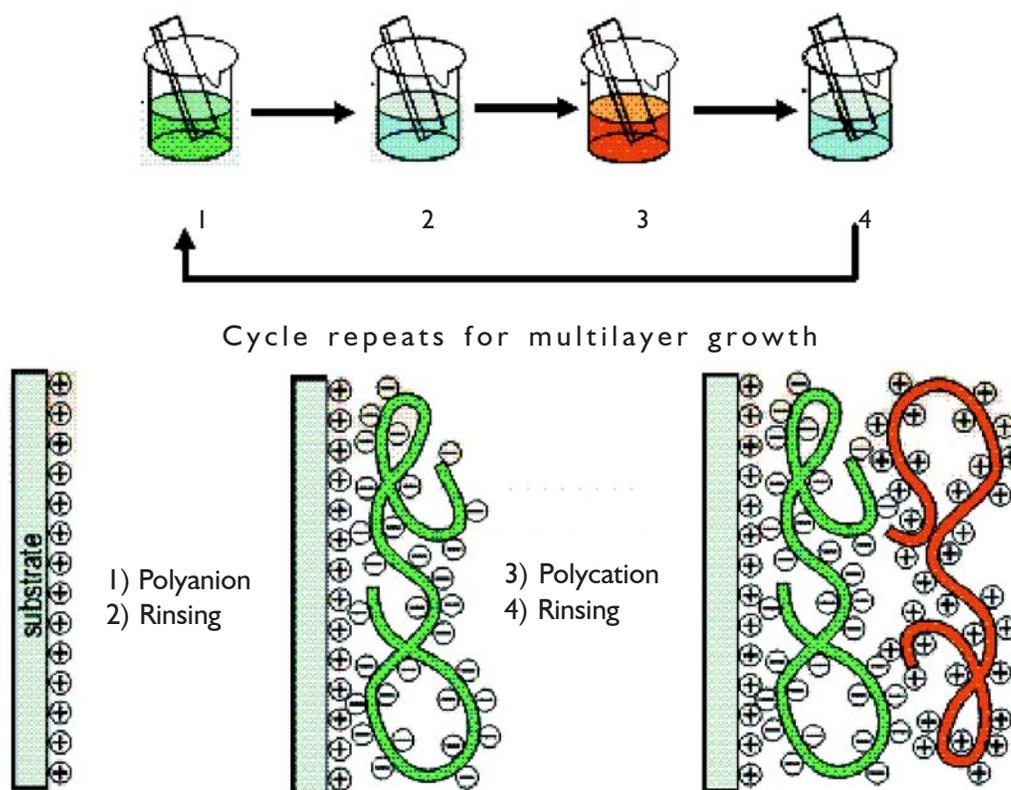


Fig. 1. Schematic representation of layer-by-layer electrostatic self-assembly process for preparation of thin films onto solid substrate

The electrostatic interaction is the main driving force for the LBL assembly, which in this case that requires the building blocks are water soluble and multi-charged species, such as poly-electrolytes, proteins and enzymes, colloidal particles, polynucleotides, organic dyes etc. Provided that the process of multilayer formation is simply based on electrostatic attraction, it does not require any potential matching of the charged groups. Therefore, we are able to incorporate more than one building block into the multilayer, and if necessary, different building blocks are incorporated in designed layer sequence. The LBL ESA deposition is independent of the size and the shape of the substrate and can be performed in an ambient condition [11]. A wide variety of materials with interesting properties have been assembled onto substrate by this unique and facile approach of film fabrication. Some important findings by various researches have been underlined in the next section.

### 3. LbL Electrostatic Self-assembled Films of Low Molecular Weight Dyes

Preparation of self-assembled molecular thin films of functional materials onto solid substrates by electrostatic adsorption technique have attracted great attention in recent times [12] because of their numerous potential applications in many fields [13]. Among the various functional molecules low molecular weight organic dyes have become technologically important materials in certain areas especially in nanotechnology and their self-assembled

structures onto solid substrates have been actively investigated for application in nanodevices [14]. Most of the small organic molecules including dyes cannot usually be assembled directly onto the substrate by LbL ESA method due to the presence of a small number of charged groups in these molecules, physisorption of such materials in LbL self-assembled films is not straightforward. The material loss by rinsing is substantial in many cases. Therefore, in most of the cases molecules having long alkyl chain or correct combination of polyions are coated onto the substrate prior to assembling the dye molecules. Various types of polyions such as poly(allylamine hydrochloride)(PAH), poly(acrylic acid)(PAA), poly(diallyldimethylammonium)(PDDA) etc. have been used by many researchers in this regard [15-17]. Self-assembled dyes have many important applications namely, laser technology, energy storage devices, printing and photography, piezoelectric devices, displays etc. [18].

However, dyes and their properties are not simple. For example, absorption and luminescence properties of their self-assembled structures in LbL films are not exactly the same as those observed for their single components. In many cases a spectral shift occurs and is highly dependent upon the assembling modes such as H-aggregates and J-aggregates [3]. In one of our earlier works [19], cationic laser dye Rhodamine-6G (R6G) has been assembled in a polymer/surfactant complex architecture. Poly(allylamine hydrochloride)(PAH) and sodium dodecyl sulfate (SDS) were used as the

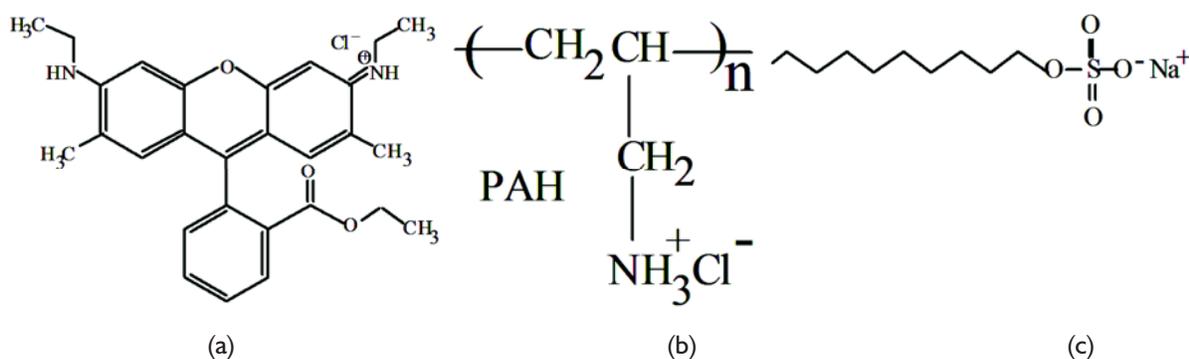


Fig.2. Molecular structure of (a) Rhodamine 6G (b) Poly(allylamine hydrochloride) and (c) Sodium dodecylsulphate

polycation and anionic surfactant respectively. Their molecular structures are shown in Fig. 2(a), 2(b) and 2(c). In aqueous solution R6G had the H-aggregates where as in complex LbL films new J-aggregates were observed and was successfully explained by UV-Vis absorption spectroscopy as shown in Fig. 3(a) and 3(b). The growth kinetics of R6G into complex LbL films was also estimated by plotting the intensity of the main absorbance peak of R6G with deposition time (Fig. 3c). In another recent work, we have successfully prepared LbL

ESA films of an anionic dye Chromotrope-2R (C2R) in the backbone of a cationic polyelectrolyte PAH. It was observed that, spectroscopic properties of PAH/C2R LbL ESA films largely depends upon the pH of the dye solution used in the adsorption process. At low pH 3, dye loading was maximum and gradually decreases with increasing pH and becomes minimum at pH 11. This is shown in Fig. 4. Atomic Force Microscopy also reveals the visual evidence for the self-assembled organization of C2R in polymeric backbone onto solid substrate.

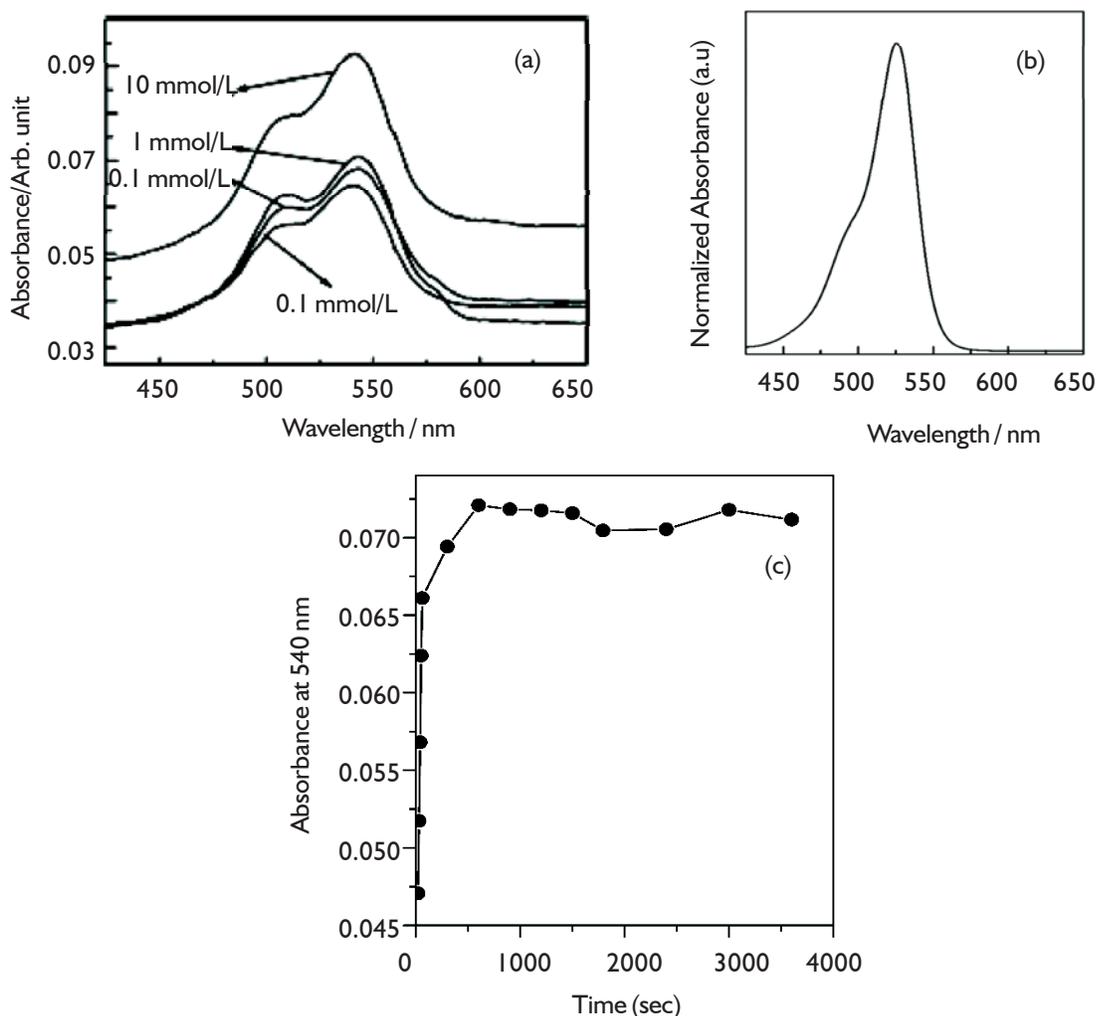


Fig.3. (a) UV-Vis absorption spectra of PAH/SDS/R6G complex LbL self-assembled films for different concentrations of SDS aqueous solution (0.01 to 10 mmol/L of SDS). (b) UV-Vis absorption spectrum of Rhodamine-6G aqueous solution (c) Absorbance intensity at 540 nm of PAH/SDS/R6G complex film vs. deposition time (Growth kinetics)(Curtsey: Chinese Journal of Chemical Physics, Vol. 24, No. 3, 2011, pp 348-352)

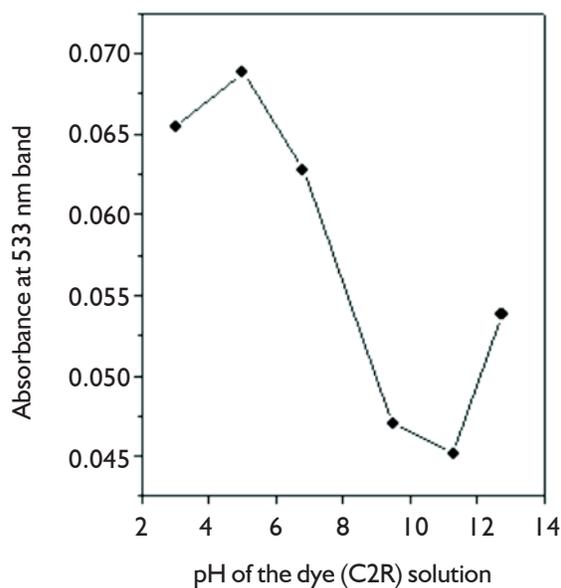


Fig.4. Absorbance intensity of 533 nm band of C2R dye in PAH/C2R LbL self-assembled film deposited at various pH of C2R aqueous solution

#### 4. Immobilization of Biomolecules by LbL ESA Method

One of the main challenges in the use of biological films or nanostructured films containing biomolecules is the preservation of the bioactivity, particularly because these films are used in their dry state. In this context, the LbL ESA method has been proven excellent for immobilization of biomolecules with preserved activity for long periods because film fabrication is performed under mild conditions and one can choose various materials as templates or scaffolds [20]. Just to illustrate the suitability of the LbL method, one may mention that tens of proteins and enzymes have been successfully immobilized by different research groups [21]. LbL films are predominantly assembled by the alternate deposition of positively charged polymers facilitated by electrostatic interaction. Among the various biomaterials, polynucleotide DNA is an interesting candidate with unique double helix structure. Immobilization of DNA onto solid substrate has profound biological advantages having a wide range of research areas including work on nanoparticle assemblies [22]. In one of the previous studies on LbL films of DNA [23] the control of the

morphology of the film was achieved by manipulating the extent of hydrogen bonding and repulsion between the negatively charged phosphate backbones. In another work, hydrogen bonding and hydrophobic interaction were used to facilitate LbL assembly of uncharged polymers [24].

In our earlier works [25] we have immobilized DNA onto the backbone of cationic polymer PAH via LbL ESA method at various temperatures. The most significant observation in our work was that once the denatured single strand DNA molecules get immobilized on the PAH backbone of the LbL films at higher temperature, they remain immobilized on the films even when the films are again taken back to the room temperature. This is manifested by the increase in the intensity of the absorption spectra of the films fabricated at higher temperature than that fabricated at lower temperature, although all the absorption spectra are taken at room temperature. It has also been observed that once the denatured single strand DNA are immobilized by PAH on the LbL films, the organization of DNA remains unaffected even after 15 days as has been evidenced by the unaltered absorbance intensity. A UV-vis absorption result (see Fig. 5a) confirms the immobilization of DNA onto solid substrate. The possible structure of DNA in PAH/DNA LbL self-assembled films is schematically shown in Fig. 5b.

An obvious application of immobilized biomolecules onto solid substrate via electrostatic adsorption is in biosensing, for their capability of molecular recognition may lead to highly-sensitive, selective biosensors [21]. Professor Osvaldo N. Oliveira Jr. at the Instituto de Física de São Carlos, Universidade de São Paulo, Brazil carried out extensive work and published a review paper on immobilization of biomolecules on nanostructured films for biosensing [26]. The variety of biomolecules and enzymes that can be immobilize onto polyelectrolyte multilayer surfaces underscores the importance of ESA as an important method for biofunctionalization. This array of molecule types includes: DNA [27], charged viral capsids [28], collagen [29], concanavalin A [30], human serum albumin (HSA)[31] and bovine serum albumin (BSA) [32].

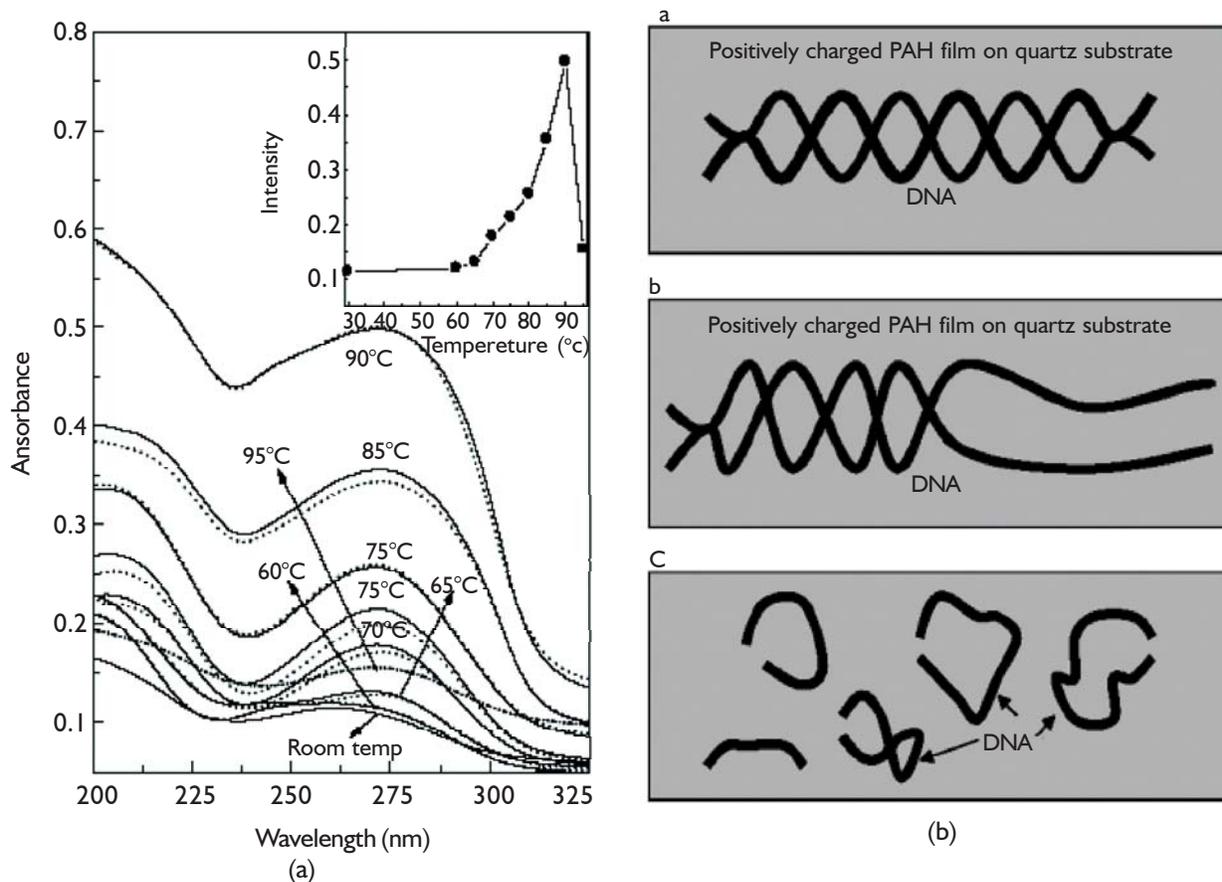


Fig. 5. (a) UV-vis absorption spectra of 1-bilayered DNA-PAH Layer-by-Layer self assembled films fabricated at various temperature viz. 60°C, 65°C, 70°C, 75°C, 80°C, 85°C, 90°C and 95°C on a preassembled PAH layer. Solid lines represent fabrication at increasing temperature; dotted lines represent fabrication at decreasing temperature. Inset shows the plot of intensity of 262 nm band as a function of time. (b) Schematic representation of the organization of DNA molecules immobilized on the PAH backbone of LbL films at different temperatures (Curtsey: Chemical Physics Letter, Vol. 450, 2007, pp 49-54)

The most important characteristic of each of these films is the marked retention of the biological activity of the biomacromolecule of interest. Caruso et al. [33] were able to immobilize Immunoglobulin G (IgG) and anti-immunoglobulin G (anti-IgG) onto a film consisting of two bilayers of polyallylamine hydrochloride (PAH) and polystyrene sulfonate (PSS). By showing that IgG would bind specifically to the immobilized anti-IgG, they demonstrated that the bound antibody retained its biological activity. Naturally occurring humic acids (HAs) have been incorporated into LbL films, with HA layers alternated with layers of a cationic polyelectrolyte. Galeska et al [34] immobilized HA in LbL films used

as semi-permeable membranes for electrochemical sensing of glucose.

### 5. Organic-inorganic Hybrid Nanostructured LbL Films by ESA Method

The electrostatic layer-by-layer (LbL) self-assembly technique has provided an effective and facile approach for the fabrication of a variety of organic-inorganic nanostructured multilayer films onto solid support with controllable architecture and properties [35]. Organic-inorganic hybrid materials are currently being the subject of intense interest in modern nanoscience as they can exhibit synergetic electrical, magnetic and optical properties

[36]. In particular, organic-inorganic composite films assembled from nanoscale building blocks with various organic and inorganic compositions possess potential applications in many areas, including microelectronics, non-linear optics, and electroluminescent devices [37-38]. This unique technique has also been extended to prepare nanolaminate thin films onto solid substrate. In a typical procedure, a flat anionic surface such as silica or mica is first covered by a molecular film of polycation by immersion in a dilute solution followed by rinsing; a layer of anionic particles is then similarly adsorbed from a dilute dispersion onto the polycationic film, and this alternating adsorption is repeated and varied as necessary to build up the nanolaminate film. Sequential adsorption has been used to prepare heterostructured films using both roughly spherical and platelike particles [39]. A recent report provided evidence for the formation of stable, water-insoluble multilayers of alternating polycations and anionic platelets of montmorillonite [40]. This polycation/clay sequential adsorption appears to be a self-healing process, with large defects in the initial adsorption step becoming gradually smoothed out with further adsorption

cycles [41]. These films have been shown to absorb moisture from the air, and have been used as humidity sensors with fast response times (a few seconds) [42]. Dr. S. A. Hussain with his group [43] recently showed the control of Froster resonance energy transfer (FRET) between two laser dyes acriflavine (Acf) and rhodamine B (RhB) using Laponite clay in LbL electrostatic self-assembled films. The schematic representation of the organization of these dyes in the host clay Laponite is shown in Fig.6 Adsorption of metal and semiconductor nanoparticles in the inorganic layer results in films with tunable optical and electro-optical properties [44-45]. A recent observation [46] of single-electron charging in a layer of gold nanospheres embedded in a complex heterostructure (effectively a nanocapacitor) demonstrates the feasibility of complex device fabrication using this relatively simple means of sequential absorption.

## 6. Conclusion

Layer-by-Layer electrostatic self-assembly is a facile and cost effective method for fabrication of molecular thin films with nanoscale control over their organization. The main driving force is the

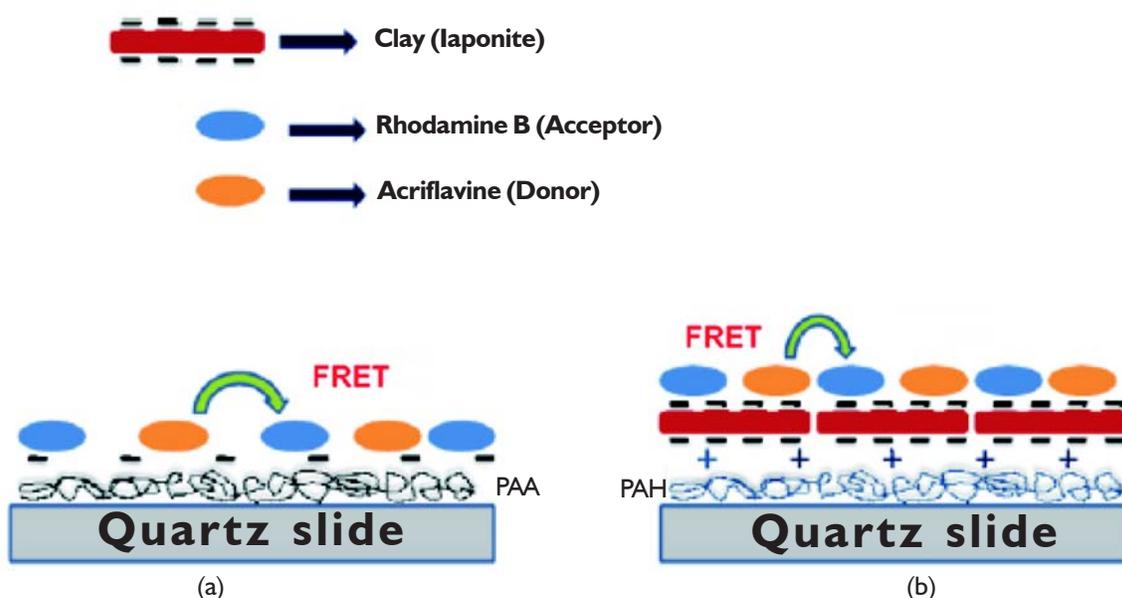


Fig. 6. Schematic representation of organizations of laser dyes acriflavine (Acf) and rhodamine B (RhB) in complex LbL film (Curtsey: Journal of Photochemistry and Photobiology A: Chemistry Vol. 252, 2013, pp. 174-182)

electrostatic interaction between the oppositely charged groups which are assembled in LbL films. Since the ESA technique involves the use of alternating anionic and cationic layers, materials that provide enhanced secondary properties can be easily incorporated, allowing control of the optical, electronic, magnetic, thermal and mechanical properties. A wide diversity of materials has been assembled in thin films using this unique and versatile technique. The formation of self-assembled structure from functional molecules namely some organic dyes having specific chromophore is of great importance in many technological applications such as non-linear optical applications, information memory and displays, printing, energy conversion and medical applications. The LbL ESA method is an excellent choice for the immobilization of biomolecules onto solid substrate with their preserved bioactivity for long periods. Additionally this method has been extended to prepare organic-inorganic hybrid nanoassemblies onto solid substrate. Many inorganic materials like semiconductor nanopartiles, clays, metal nanoparticles, porous inorganic materials are suitable for film fabrication by this method. In contrast to Langmuir-Blodgett films, substrates of any size or shape may be coated uniformly on all surfaces. Avoiding high temperature processes allows multilayer coatings to be created on nearly any solid substrates, including plastics, semiconductors, organic films, ceramics or metals, without degrading or destroying the substrate.

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