

Study of the non-covalent interactions in Langmuir–Blodgett films: An interplay between π – π and dipole–dipole interactions

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Abstract

This work describes Langmuir–Blodgett (L–B) monolayer and multilayer assemblies constructed from a series of NLO-active azo-benzene derivatives possessing terminal moieties of variable dipole moment. The terminal groups are electron acceptors (acetyl, nitro, and cyano) and are connected to a common amphiphilic azo-benzene segment. Our experimental and theoretical results show that the interplay between two dominant non-covalent interactions within the assemblies, namely dipolar and π – π stacking interactions, dictate the packing density, structural order, as well as the electronic properties of the final films. L–B films of the acetyl derivative, which has the weakest total dipole across the azo-benzene chromophore, exhibits the highest packing density and the largest blue shift in the UV–visible absorption spectrum. This is rationalized by relatively strong π – π interactions between the azo-benzene chromophores overwhelming weak intermolecular dipole–dipole interactions. More importantly, the small internal dipole in the acetyl functional groups encourages packing in a configuration that lowers the overall energy and increases the packing density. In the case of the cyano and nitro derivatives, both L–B films show decrease in packing density and a weaker electronic coupling due to unfavorable overall dipole interaction that offsets the π – π interaction. We show that such unfavorable interactions lead to the formation of a staggered and loosely packed configuration. Our work demonstrates that a subtle difference in molecular structure can have a dramatic impact on aggregation, and consequently on the electronic and optical properties of nano-assemblies. This work demonstrates a way of controlling the formation of nanoscale structures at the molecular level through the control of noncovalent interactions.

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1. Introduction

Understanding the intrinsic structure–property relationships in highly ordered molecular assemblies has been underscored by developments in organic electro-optic materials [1–4]. Despite some shortcomings, self-assembly methods continue to hold a lot of promise in achieving desired architectures in organic assemblies. The desire to guide molecular assembly into hierarchical

macro-structures has been propelled by the realization that specific molecular geometries favor specialized functions, such as the nonlinear optical (NLO) effects observed in asymmetrically ordered multilayers [5,6]. For example, NLO-active organic materials containing asymmetric chromophores have characteristics (e.g. low dielectric constants, ultrafast response times, and large hyperpolarizabilities) that make them an attractive alternative to their inorganic counterparts [7–9]. However, achieving the inherent intralayer asymmetric alignment in self-assemblies has proven challenging largely because interactions within such assemblies are poorly understood.

Perhaps the most extensively used method of directing molecular orientation in multilayers is the Langmuir–Blodgett

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(L–B) technique, in which compressed amphiphilic molecules at the air–water interface are reversibly transferred to a solid support [10]. Despite considerable experimental and theoretical efforts, fabricating uniform, defect-free films with predictable structural properties continues to pose a significant challenge [11,12]. Although the L–B technique has produced a plethora of systems containing chromophoric units derived from stilbenes, merocyanines, hemicyanines, azobenzenes, the ultimate goal of precise control over the chromophore orientation is yet to be demonstrated [13,14].

One major hurdle in achieving long-range order is chromophore randomization at the mesoscale. Our previous work has shown the presence of significant inter-layer mixing between L–B layers resulting in structural defects and chromophore tilting that becomes amplified as a function of bilayer number [15]. Moreover, fatty acid spacers, such as stearic acid, may be used to maintain noncentrosymmetry throughout the bulk film. However, these spacers have been observed to augment disorder in some L–B films since stearic acid may form two-dimensional crystalline structures resulting in a heterogeneous monolayer filled with defects [16]. More importantly, staggered molecular structures may form due to repulsive interaction between strong dipoles. One way to combat these effects and to increase order is to promote the formation of ordered aggregates. For example, Li et al. achieved noncentrosymmetric aggregates on L–B films using a stilbazolium dye dimer whose monomeric units are connected with a methylene bridge [16]. The observed NLO response of the resulting L–B films was found to be greater than that of the L–B film consisting of the monomer formed under similar experimental conditions. Despite enormous efforts in controlling the experimental parameters, such as temperature and surface pressure, the intrinsic intralayer disorder caused by unfavorable dipole–dipole interactions between NLO amphiphiles and interlayer interactions, inhibit the formation of 3D structures with long range order. It appears that the interplay between enthalpy and entropy, and the nature of non-covalent forces that unite molecular building blocks to form self-assembled aggregates need to be understood. To address some of these issues, we have synthesized a series of NLO-active molecular building blocks that are amphiphilic, of approximately the same size, and have terminal dipole moieties of variable electron-withdrawing strength. Understanding how non-covalent interactions (e.g. Coulomb forces and π – π interactions) influence the structure and order of the functional nanoassemblies forms the central theme of this paper. Understanding these interactions could allow one to predict equilibrium structures and properties of functional nanoassemblies based on the specific amphiphilic structure.

Intermolecular aggregation within 2D assemblies can lead to two arrangements for adjacent chromophores aligned parallel to each other. A “head-to-head” and “tail-to-tail” arrangements of the dipoles lead to so-called H-aggregates. Their optical absorption spectra display prominent spectral blue shifts in the absorbance compared to the monomeric units. On the other hand, J-aggregates are formed when dipoles are arranged in a “head-to-tail” configuration, leading to red shifts in the linear

absorption [17]. This work describes the L–B assembly on a hydrophobically rendered quartz substrate and characterization of the class of NLO-active amphiphiles X-azo-(CH₂)₁₀-SO₃[−], where X = −COCH₃, −NO₂, or −CN (Fig. 1). These molecules contain the essential functional groups (electron donor and acceptor groups bridged by an azo-benzene group) required for a large second order hyperpolarizability. We have recently reported the large second harmonic response from multilayer systems comprised of these amphiphiles [18]. Absorption spectroscopy studies revealed H-aggregate [19] formation of X-azo-(CH₂)₁₀-SO₃[−] in films assembled using electrostatic self-assembly (ESA) with oppositely charged polyelectrolytes. It is believed that the head-to-head packing of the chromophore was promoted by the presence of inter-alkyl chain interactions and the anchoring of the SO₃[−] head groups of the surfactants into the underlying hydrophilic polycationic layer [18].

The work presented here further explores dipolar interactions on aggregate formation in L–B assemblies of X-azo-(CH₂)₁₀-SO₃[−]. Thus, this study provides valuable insight into the design of molecular building blocks that could lead to structures with desirable nonlinear optical and electronic properties. Curiously, in the multilayered films formed by ESA, the blue shift reflecting the degree of H-aggregation increased with strength of the molecular dipole moment, μ as follows −COCH₃ < −NO₂ < −CN. Given the same “head-to-head” (“tail-to-tail”) molecular stacking, the strength of dipolar interactions between chromophores will directly affect the excited state shifts of the aggregate. However, we show that an opposite trend emerges in the absorption spectra of the L–B films of X-azo-(CH₂)₁₀-SO₃[−] adsorbed onto a hydrophobic substrate compared to their spectra in chloroform solution. Furthermore, pressure–area (*P*–*A*) isotherms and hysteresis studies were used to explore the packing density and aggregation properties of the L–B films. We observe that the packing density of monolayer structure at the air–water interface is the highest for acetyl-azobenzene (X = −COCH₃), followed by nitro-azobenzene (X = −NO₂) and cyano-azobenzene (X = −CN) amphiphiles. This result is congenial to the

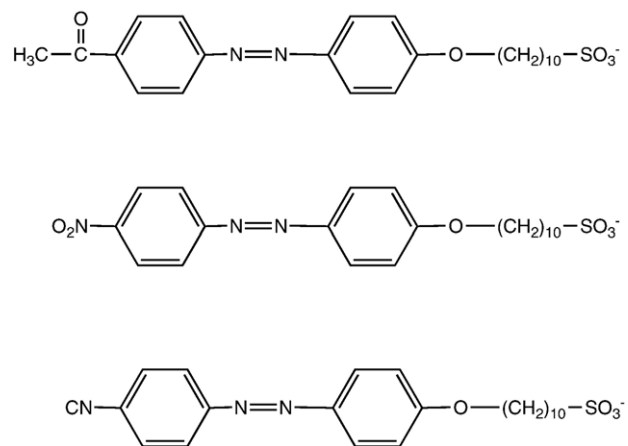


Fig. 1. Structure of the three NLO-active amphiphiles used in this study. The various terminal electron withdrawing groups (X) are shown (−COCH₃, −NO₂, and −CN). The dipole moment of the X group follows the order −COCH₃ < −NO₂ < −CN.

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