

# Control synthesis of functional nanoassemblies using Langmuir-Blodgett method

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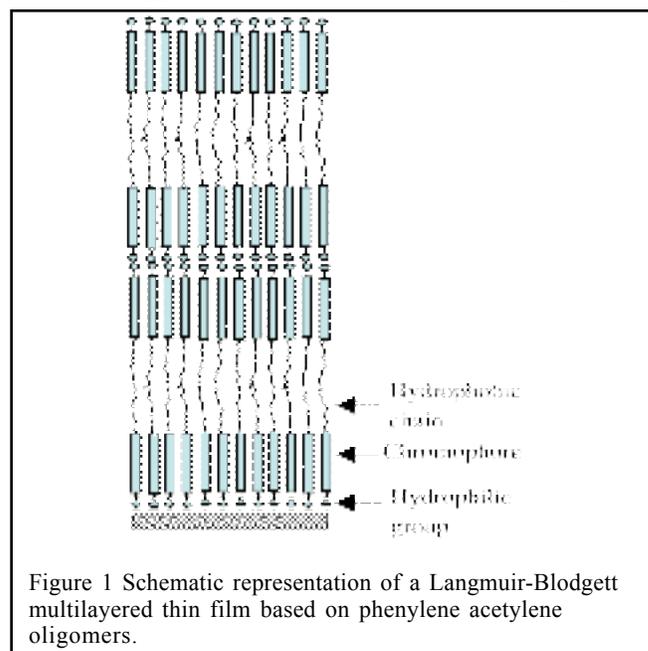
**Abstract** — We reported here design syntheses of a series of amphiphilic molecular building blocks that can self-assembled at the air-water interface to form 2D and 3D nanostructures with tunable opto-electronic properties. Compression of these molecular building blocks with tunable  $\pi$ - $\pi$  (hydrophobic) interactions using Langmuir-Blodgett method gives rise to monolayer thin films with different packing density and electronic coupling between chromophores. Depends on the noncovalent interaction between chromophores, we observe a transition of packing density with increasing sized of phenylene acetylene repeat unit. Furthermore, we use a series of spectroscopy tools such as neutron scattering to probe the nanoassembly structures at the molecular level. We also use simulation method to help determine the excited state electronic structure. Our results demonstrate that the interplay between dipole-dipole and  $\pi$ - $\pi$  interactions dominate the formation of thin films with various packing density and their associated optical properties.

**Index Terms** — Langmuir, self-assembly, noncovalent interaction, phenylene acetylene, oligomer

## I. INTRODUCTION

Recent efforts to improve the efficiency and functionality of modern materials have shifted the focus of scientific inquiry increasingly toward the nanoscale domain. In the area of nanoscale optical science, processes and structures smaller than the wavelength of optical radiation have been constructed for the confinement of radiation and for influencing photochemical transformations. The ability to control the orientation of molecules becomes especially important when contemplating the construction of nonlinear optical (NLO) materials and tunable optoelectronic devices.<sup>1-3</sup> In this respect, the assembly of non-centrosymmetric structures is of importance. Langmuir-blodgett method is the most commonly used technique to organize amphiphilic molecules into densely packed 2 D structure at the air-water interface. The 2D structure can then be transferred to the substrate. Ordered 3D nanostructures can then be obtained by repeating this process until the desired thickness is achieved. If the structural order is retained throughout, we can then achieve a sum effect of the functionality represented by individual layer. In the case of nonlinear optics, if donor-acceptor chromophores were organized in such a way that dipole moments were orientated in

the same direction, we will observe quadratic increases of second harmonic signal with increasing film thickness (number of bilayers) as predicted by theory.<sup>4</sup> Another example is the use of molecules that fluoresce to form multilayer structure.<sup>5,6</sup> The quantum efficiency and the overall luminescence are dominated by the intralayer structure (packing density) and the wavefunction overlap between two layers. Therefore, the idea of relying on the sum effect of individual LB layers to obtain an enhanced functionality in 3D materials has to be carefully orchestrated because recent study shows intermixing between layer caused by entropy and defect structure at the previous layer could have huge impact in the overall thin film properties.<sup>7</sup> In fact, a perfectly discrete layer constructed by LB method whether being x-type or y-type is yet to be seen. The main reason responsible for the disorder in the self-assembly materials is believed to be a lack of in-plane order due to unfavorable dipole-dipole interaction. As the amphiphiles were brought together at the air-water interface by increased surface pressure, the amphiphiles formed a staggered structure to accommodate the dipoles



resided at the end of the amphiphiles. Such staggered structure is well manifested by the X-ray reflectivity measurement of monolayer at the air-water interface. As

we transfer the staggered structure from the air-water interface to the substrate, the interactions between layers may have caused further amplification of disorder and intermixing as evidenced by the neutron and X-ray scattering data.

In a typical deposition cycle using self-assembly method involved one or more than one species (Figure 1), materials from a given deposition cycle may occupy defects in underlying layers, and that the material from either species will spread out in the direction perpendicular to the substrate, leading to enhanced interpenetration, despite the maintenance of equivalent bilayer thicknesses over many layers. In other words, equivalence in deposition amount and thickness over many layers may indicate similar net surface conditions in each layer, but care must be taken in using the notion of a similar surface to infer consistency in molecular order within layers. Even disordered systems can display seemingly regular deposition patterns—a film with disorder on the molecular level may appear markedly ordered at the macroscale. Such considerations are far reaching, in a field largely focused on not only the order but also the chromophore orientation at the molecular level.

Our earlier study suggests that 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 structure with long range order.<sup>8</sup> It seems that the interplay between enthalpy and entropy, the nature of non-covalent forces that connect the molecules in self-assembled aggregates are yet under our control. To try to address the above issues, we strive to design synthesis of novel molecular building blocks that are linear, have a minimized dipole-dipole interaction and tunable non-covalent interactions aiming at reducing the intralayer defects hence decreased interpenetration between layers. Our goal is to achieve greater understanding of how interplay between electrostatic, entropy and non-covalent interaction (e.g. Van der Waals force and  $\pi$ - $\pi$  interactions) dominate the structure and order of the functional nanoassemblies.

## II. EXPERIMENTAL SECTION

### Langmuir film

$4.0 \times 10^{-3}$  mmol phenylene-ethynylene oligomers were dissolved in 10 ml chloroform which leads to a 0.4 mM solution. Approximately 0.5 ml of these as-prepared chloroform solutions is spread on top of the water surface. The measurements of the surface pressure-area ( $\Pi$ -A) isotherms were carried out using a

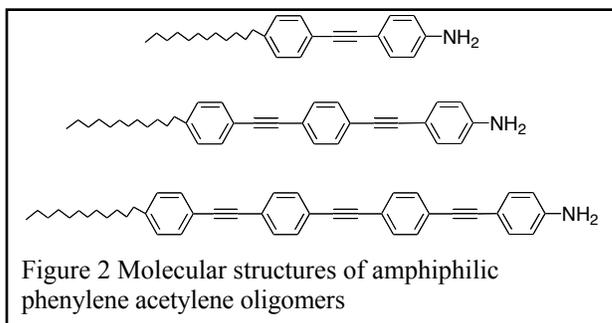
KSV 2000 standard L-B trough (KSV Instrument, Helsinki, Finland) with a Wilhelmy-type balance, Teflon trough and symmetrical hydrophilic Delrin barriers. The system was controlled by a computer, the trough was set in an enclosure to be protected from dust and drafts, and the temperature was controlled to within  $\pm 0.5^\circ\text{C}$ . Ultrapure water (resistivity greater than 18 M $\Omega$  cm) from a Barnstead e-pure system was used as the subphase. Monolayers were spread from chloroform solutions on ultra pure water subphase at 21 $^\circ\text{C}$ . After waiting for 15 min to allow solvent evaporation, isotherms were obtained by reducing the surface area available to the material at a rate of 10 cm<sup>2</sup>/s. During the depositions, the transfer surface pressure was fixed at 25 mN m<sup>-1</sup>.

All substrates were cleaned by immersion in a 7:3 mixture of concentrated sulfuric acid and 30% H<sub>2</sub>O<sub>2</sub> at 80 $^\circ\text{C}$  for 1 hour (Piranha etch treatment). Prior to use, substrates were treated with octadecyltrichlorosilane (OTS, 1% in hexadecane solution) at 40 $^\circ\text{C}$  for 45 min and washed thoroughly in CHCl<sub>3</sub> in order to generate a hydrophobic surface.

FT-IR spectra were recorded with a Mattson spectrometer by mixing the molecules in the KBr matrix or drop casting methylene chloride solution on top of the KBr window. <sup>1</sup>H and <sup>13</sup>C spectra were recorded with a Broker 500 MHz spectrometer. Chemical shifts are given in parts per million ( $\delta$ ) relative to tetramethylsilane. UV/Vis absorption spectra were taken with a Cary 500 Scan UV-Vis-NIR spectrophotometer. Fluorescence measurements were recorded on a Jobin Yvon Fluorolog3 spectrometer.

## III. RESULTS AND DISCUSSIONS

The delicate balance between electrostatic forces and non-covalent interactions govern the formation of amorphous and ordered thin films with its associated properties. We have synthesized a series of amphiphilic phenylene acetylene oligomers which may enable us determine the following : 1) enhanced noncovalent ( $\pi$ - $\pi$ ) interaction between amphiphiles with increasing intralayer order by forming aggregates 2) probe the structure and packing density with optical spectroscopy.



In addition, the structure property relationship at the nanoscaled can be realized as we construct the 3D materials with the bottom up approach.

Noncovalent interactions between amphiphiles are of central importance in determining the layer interactions which can be fine-tuned by changing the structure of the chromophore.<sup>9</sup> The 2D structure and packing density of the monolayer at the air-water interface can be determined by the transfer ratio and the pressure isotherm measured at a specific temperature. Monolayer and multilayer Langmuir–Blodgett thin films based on these molecular building blocks with minimized dipole-dipole interactions will be determined by UV-Vis, ellipsometer and fluorescent spectroscopy.

The molecules of interest are shown in Figure 2. Amphiphilic phenylene acetylene dimer, trimer and tetramers are prepared by coupling reaction using Pd catalyst. We start off by measuring the optical properties of these phenylene-acetylene oligomers and using time-

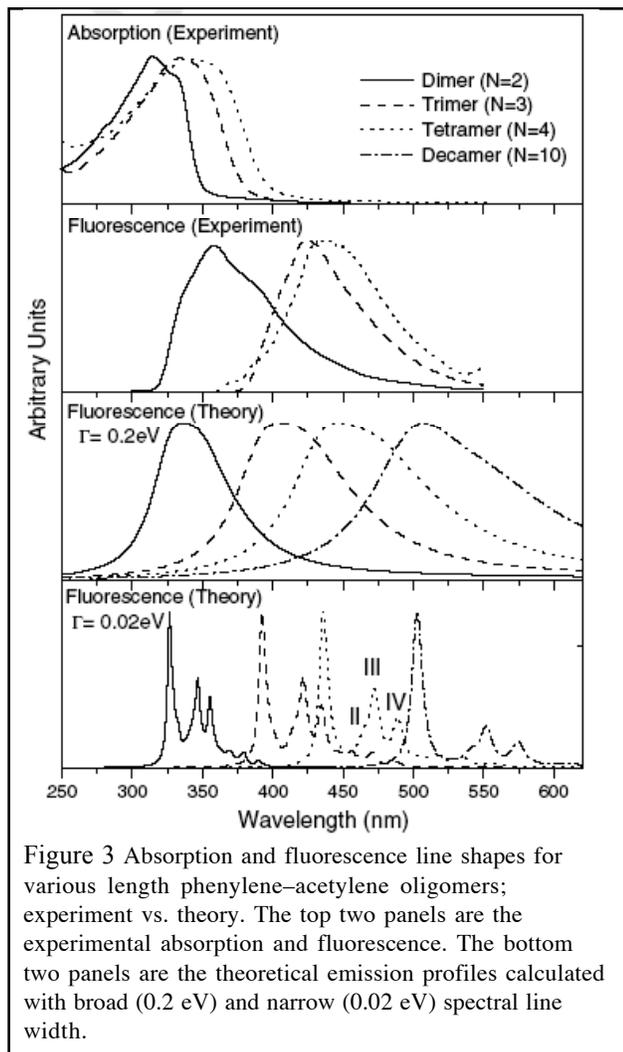


Figure 3 Absorption and fluorescence line shapes for various length phenylene-acetylene oligomers; experiment vs. theory. The top two panels are the experimental absorption and fluorescence. The bottom two panels are the theoretical emission profiles calculated with broad (0.2 eV) and narrow (0.02 eV) spectral line width.

dependent density functional theory approaches to calculate their excited state electronic structures. The absorption and emission spectra of these oligomers measured via experimental and theoretical methods are shown in Fig. 3. Our results clearly show that experimental absorption-fluorescence spectra are nearly mirror-image profiles; this indicates the same nature of the absorbing and emitting electronic state. The last two panels are theoretical results calculated with broadening parameters of 0.2 and 0.02 eV, respectively. The larger broadening is able to model experimentally measured line shapes. In-deed, we observe good overall comparison between theory and experiment. In particular, the shoulder on the red-side of all spectra are well reproduced. One very important result of this study is to show the geometric effect which governs the conjugation length of oligomers. Trimer appears to have a relatively better planarity between three benzene rings as compare to dimer and tetramer. With this understanding in mind, we move to study structure and properties of these oligomers at the air-water interface.

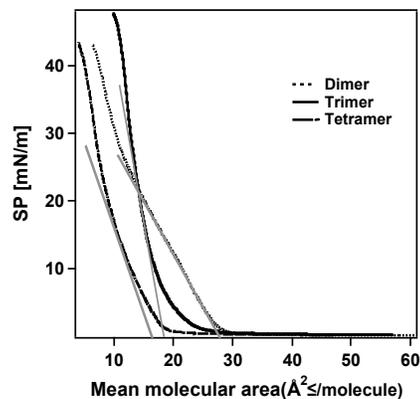


Figure 4 Pressure-area isotherms of phenylene acetylene dimer, trimer, and tetramer measured at room temperature.

As we organize these molecules at the air-water interface, surface-pressure isotherms measured at room temperature exhibit a typical phase transition from gas phase to liquid-expanded, to liquid-condensed state for all three oligomers. It is even more interesting to see the area/molecule (determined as the intersect between the tangent line of liquid-condensed state to the X-axis) is largest for dimer, and smallest for tetramer (see Fig. 4). The area/molecule for phenylene acetylene dimer, trimer and tetramer are 28, 18, and 16 Å<sup>2</sup>, respectively. Although the relative size of these three oligomers has yet been determined, it is likely that dimer is smaller than trimer and trimer is smaller than tetramer. The smallest area/molecule at the air-water

interface is however contrast to the order of the size of the chromophores. This can be understood as the denser packing of tetramer is driven by the stronger  $\pi$ - $\pi$  interaction between chromophores. Since the size of individual molecule does not significantly differs from one another, as the molecules come together with increasing surface pressure, tetramer with longer phenylene acetylene repeat unit has a stronger  $\pi$ - $\pi$  interaction that draws the molecules closer to form densely packed layer structure. The hydrophilic group in these oligomers is a primary amine. Lacking an acceptor group on the other end of the chromophore, we

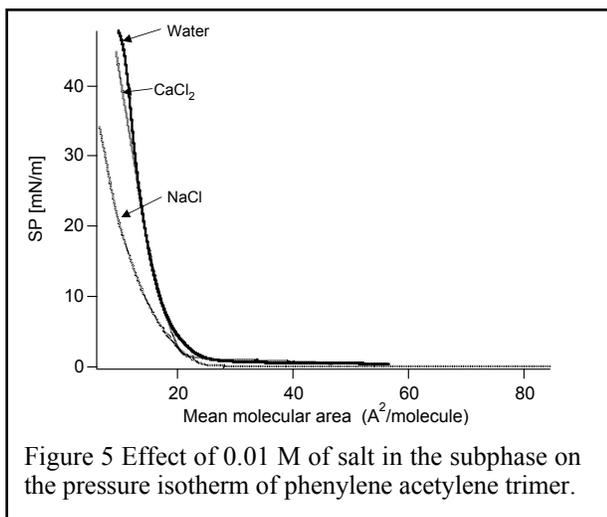


Figure 5 Effect of 0.01 M of salt in the subphase on the pressure isotherm of phenylene acetylene trimer.

expect to have a minimized dipole moment which has basically minimized influence on the overall structure and properties. We believe the unfavorable interaction between amine head groups is overwhelmed by the  $\pi$ - $\pi$

interactions between chromophores. Another approach to further mitigate this unfavorable interaction is to disperse salt in the subphase. These counter ions at the interface appears to have significant impact on the packing of the oligomers at the interface. Figure 5 shows the pressure isotherms of phenylene acetylene trimer measured in the presence of two different salts, NaCl and CaCl<sub>2</sub>. The addition of NaCl to the subphase has shifted the isotherm to the smaller area/molecule which suggests a denser packing between trimer molecules presumably due to the counter-ion effect. This is consistent with previously reported result which show structural modification upon addition of counterions.<sup>10</sup> Up to this pint, we have yet discuss the hydrophobic (Van der Waals) interaction between long alkyl chains. We assume it contributes to some extent to the formation of overall structure.

The monolayer and multilayer Langmuir-Blodgett films is fabricated by repeatedly transferring the structure from the air-water interface to the substrate. Thin films prepared from phenylene acetylene oligomers show significant fluorescence quenching presumably due to self-quenching from the close packed layer structure. The fluorescence quenching is tunable by varying the surface pressure, hence the packing density of the monolayer and multilayer thin film. The above results validate our hypothesis that noncovalent interactions between chromophores whether being dipole-dipole,  $\pi$ - $\pi$ , or Van der Waals interaction could have a huge impact on the packing density, subsequently the optical properties of the final structures.

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