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X23B

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Nanoscale Self-Assembly of Thin-Film Molecular Materials for Electro-optic Switching

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Scientists from Northwestern University in Evanston, Illinois and the Weizmann Institute of Science, Rehovot, Israel, have devised a two-step assembly technique to make highly ordered, intrinsically acentric organic materials which can be integrated into electro-optic (EO) and related devices, such as light modulators and switches. The scientists have shown that the self-assembled photonically/electronically functional materials are competitive in terms of EO responses with the highest efficient polar films reported to date, and are more efficient than inorganic systems, such as LiNbO_3 .

Forming nanoscale organic films and integrating them into semiconductor electronics and all-organic microphotonic circuits has stimulated intense academic and industrial research, but progress is hampered by the lack of device-quality functional molecule-based thin films, driving the need for new reliable film-growth methods.

A general applicable method has been developed generating thermally robust multilayered materials. This new synthetic approach involves two alternating deposition steps, as shown in Figure 1. First, monolayers (one-molecule-sized layers) of chromophores are co-

valently bound on hydrophilic substrates (step (i)). The siloxy removal step (ii) renders the surface hydrophilic, thus allowing the rapid build-up of a covalently-bound siloxane-based capping layer. The resulting films are intrinsically

acentric, so no post-deposition steps such as high-voltage poling to align the molecular building blocks are necessary, as in other film growth techniques.

We have developed a film growth process based on chemically reliable steps, amenable to automation-by using a single reaction vessel or dip-coating - and allowing an excellent control of material properties - which is of great interest for optical telecommunications and electronic applications. The high degree of control over film dimensions, texture, and properties has been unambiguously demonstrated using various physico-chemical analytical tools, including second harmonic generation measurements and synchrotron x-ray reflectivity measurements (XRR) performed at NSLS beamline X23B (Figure 2).



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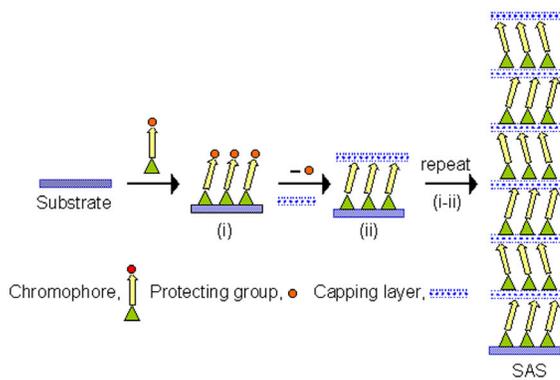
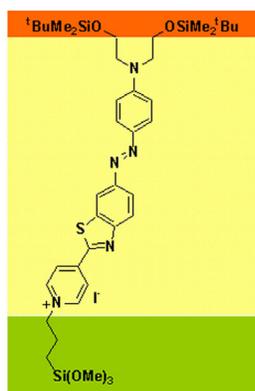


Figure 1. Two-step layer-by-layer self-assembly process generating intrinsically acentric superlattices.

The XRR experiments afforded crystal-clear structural information on the chromophore density ($\sim 50 \text{ \AA}^2/\text{chromophore}$), film thickness ($\sim 2.8 \text{ nm}$ for each chromophore + siloxane-based capping layer), and surface morphology. The robust

capping layer is $\sim 8 \text{ \AA}$ thick. The streamlined two-step assembly process shown in Figure 1 could be extended to a wide range of molecular building blocks, and become a major synthetic route for the formation of various functional sub-

micrometer-sized solids with superb control of material characteristics at the nanoscale level. This assembly process is also part of an ongoing investigation aimed at creating "all-organic" electro-optical modulators (Figure 3).

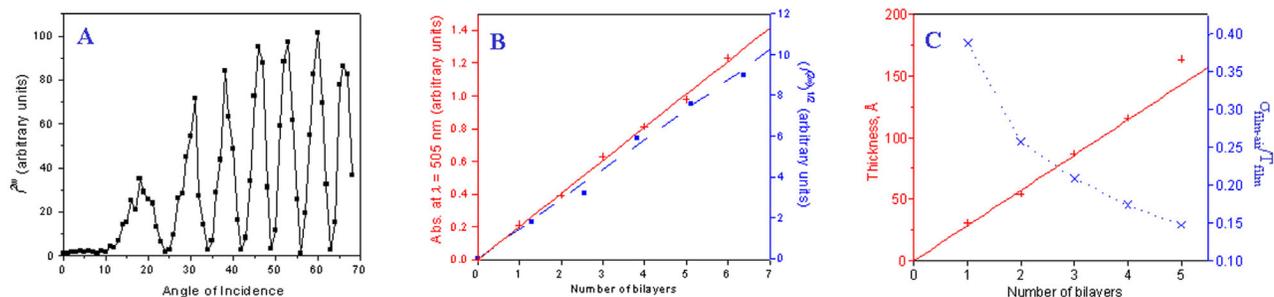


Figure 2. (A) Second harmonic generation response at $\lambda_o = 1.06 \text{ \mu m}$ as a function of fundamental beam incident angle from a float glass slide having a polar monolayer on either side. (B) Optical transmission and second harmonic generation as a function of the number of bilayers. Left y-axis: absorption at $\lambda_{max} = 505 \text{ nm}$ (+). Right y-axis: square root of the SH intensity (•). (C) Specular X-ray reflectivity measurements. Left y-axis: film thickness (\AA) as a function of the number of bilayers (+). The solid line is the fit by linear regression for 1-4 bilayers, indicating $T = 28.6 \pm 0.6 \text{ \AA} \times n$. Right y-axis: relative film roughness, $\sigma_{\text{film-air}}/T_{\text{film}}$, as a function of the number of bilayers (x). The dotted line is drawn as a guide to the eye.

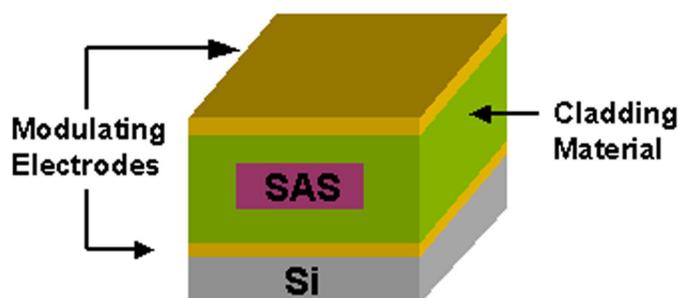


Figure 3. Schematic view of a prototype "all-organic" electro-optical modulator based on intrinsically acentric self-assembled superlattices (SAS). Commercially available polymers such as Cyclotene™ and/or Cytop™ can be used as cladding layers.