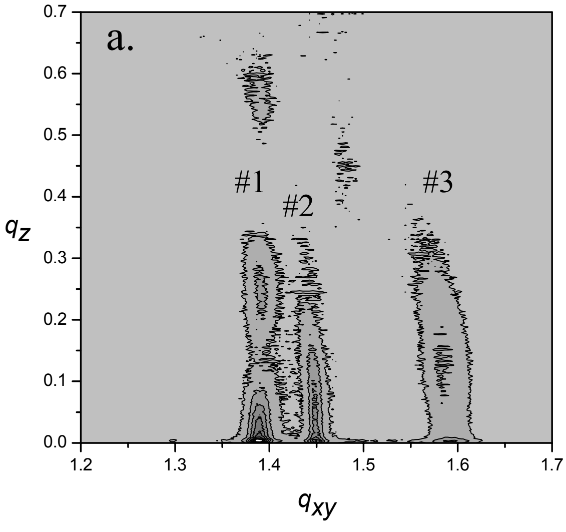
ESRF	**Experiment title:** **Oriented nucleation of CdS and PbS nanoparticles at conjugated polymer interfaces**	**Experiment number**: HS-2035
Beamline: ID-10B	**Date of experiment**: From: 30/04/2003 to: 06/05/2003	**Date of report**: 25/07/2003
Shifts: 18	**Local contact(s):** Dr. Oleg Konovalov	***Received at ESRF***:

Names and affiliations of applicants (* indicates experimentalists):
Dr. Yuval Golan*, Dept of Materials Engineering
Dr. Amir Berman*, Dept of Biotech. Engineering
Mr. Yevgeniy Lifshitz*, Dept of Materials Engineering
Ben-Gurion University of the Negev, Beer-Sheva 84105, ISRAEL

1. GIXD studies of the structure of ultrathin polydiacetylene films at the air-water interface.
The first experiments in HS-2035 were devoted to the study of the structure of the linear ultrathin polydiacetylene substrate at the air-water interface.
10,12 Pentacosadiynoic acid molecules were spread on water, compressed to a trilayer structure and exposed to UV radiation. After the topochemical polymerization the GIXD measurement showed the following pattern as shown in Fig. 1a. Table 1 summarizes the data in real and reciprocal space. The Bragg rod intensities as a function of q_z are plotted separately in Figs. 1(b-d).



Peak#	q_{xy} [A^{-1}]	q_z[A^{-1}]	d[A]	d*[A]	*hk*
1	1.3834	0	4.54	0.2203	10
2	1.45	0.11	4.33	0.2308	01
3	1.575	0.12	4.0	0.2499	1-1

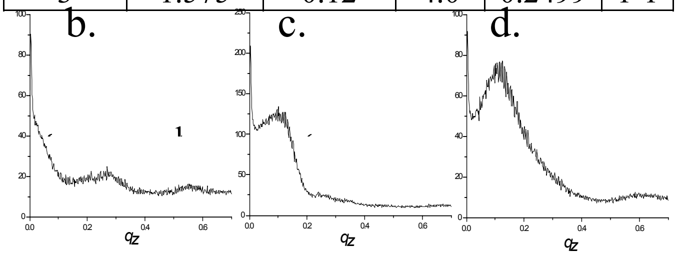


Figure 1. (a) Diffraction intensity map of q_z vs. q_{xy} obtained in a GIXD experiment from PDA trilayer on air-water interface. (b-d) Bragg rods for the three observed peaks: (b) Bragg rod at 1.383 A^{-1} (#1). (c) Bragg rod at 1.450 A^{-1} (#2). (d) Bragg rod at 1.575 A^{-1} (#3).

Table 1. Summary of GIXD diffraction data from the three fundamental peaks obtained for PDA spread, compressed and polymerized on pure water**.**

The GIXD results were interpreted into a crystallographic model describing the PDA arrangement on the air-water interface (Fig. 2). The oblique unit cell was represented as a (distorted) centered rectangular cell in order to allow direct comparision with the previously published electron diffraction (ED) data by Kuriyama, Kikuchi and Kajiyama [*Langmuir* 14 (1998) 1130]. A good agreement was obtained between our GIXD data and the reported ED results.

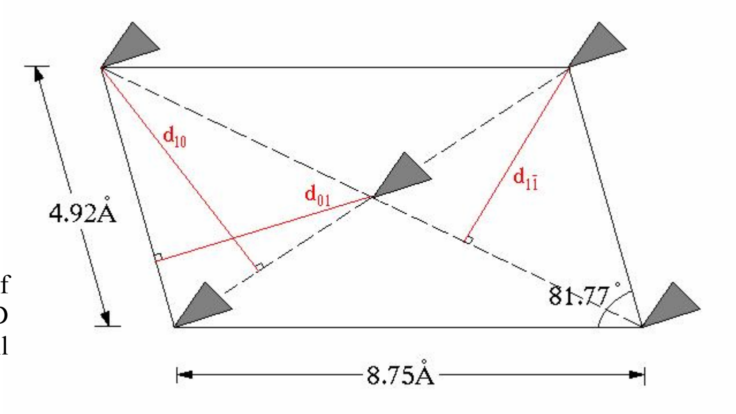


Figure 2. Schematic representation of the unit cell deduced from the GIXD data obtained in this experiment. Cell area: A=42.6A^2; tilt angle: τ~5^o.

Note that the 4.9A is the theoretical distance for the conjugated system in the backbone direction, as expected for this material.

2. GIXD studies of polydiacetylene films with various divalent metal cations present in subphase.

While the basic structure of the 2D PDA crystals remained essentially the same, pronounced effects of the subphase composition were nevertheless observed as a function of the cations present in solution. A gradual shift of the (10) Bragg peak to smaller q_{xy} values is shown in Fig. 3. The tendency is consistent with the radii of the cations present in the subphase (H^+<Zn^{2+}<Cd^{2+}<Pb^{2+}). This confirms that, as expected, the PDA film is strongly interacting with the cations in the subphase. Moreover, the PDA structure is clearly affected by the cations in the subphase, providing a unique and potentially technologically useful "self-adjusting" property of the PDA films as templates for epitaxy of the corresponding nanocrystalline semiconductors.

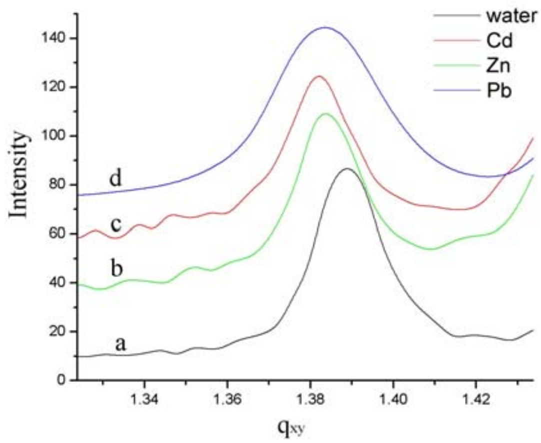


Figure 3. (10) GIXD peak obtained on (a) pure water subphase. (b) 0.3 mM Zn^{2+} subphase. (c) 0.3 mM Cd^{2+} subphase. (d) 0.3 mM Pb^{2+} subphase.

3. GIXD studies of CdS nanoparticles directly deposited on polydiacetylene films at the air-water interface

Direct deposition of CdS nanoparticles on PDA at the air-solution interface was carried out in experiment SI-785 and was repeated as a reference for the current series of experiments. The results turned out to be highly reproducible and all conclusions from SI-785 were reconfirmed in the reference measurement.

4. GIXD studies of PbS nanoparticles directly deposited on polydiacetylene films at the air-water interface

The GIXD experiment of direct deposition of PbS nanoparticles on PDA indicated the coexistence of two discrete orientations: (i) Reflections corresponding to <100> $_{PbS}$ oriented nanoparticles marked "1" and (ii) Reflections corresponding to <111> $_{PbS}$ oriented nanoparticles marked "2" in Fig. 4a. These results are supported by high resolution TEM (HRTEM) results that confirmed the coexistence of these orientations (Fig. 4b,c). The arrows indicate the linear conjugated direction in the PDA substrate film.

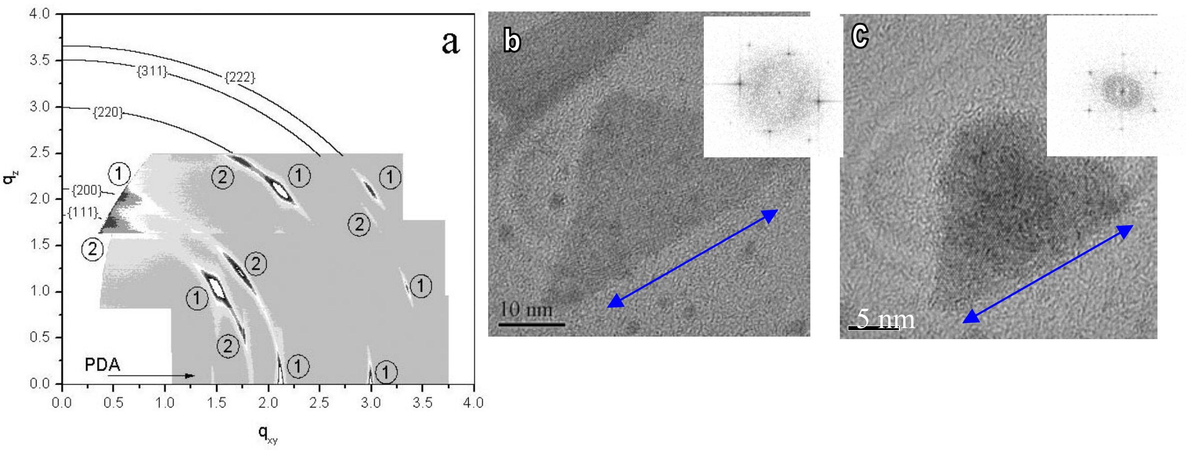


Figure 4. (a) GIXD of PbS nanoparticles on PDA at the air-solution interface. The arcs indicate theoretical position of rocksalt PbS rings according to JCPDS file. Reflections from PDA are marked with an arrow. (b,c) HRTEM images of PbS nanoparticles: (b) A right-angle faceted crystal characteristic of the <100>$_{PbS}$ orientation. (c) An equilateral triangular shaped nanocrystal characteristic of the <111>$_{PbS}$ orientation. The blue arrows represent the conjugated direction of PDA that is found to be parallel to <110>$_{PbS}$ in all cases.