



**The Norman Seiden Multidisciplinary Graduate Program  
in Nanoscience & Nanotechnology**

Seminar lecture

Faculty members, students and the general public are hereby invited to a seminar given  
by

**Nitai Arbell**

The Multidisciplinary Program for Nano Sciences and Nano  
Technology

Doctoral thesis on

”Enantioselective Photocatalysis - Design,  
Synthesis and Characterisation of a Composite  
Photocatalytic System for Chiral Separation”

which will take place on *Wednesday, 5.2.25, at 13:30*

in Hall no. 6 at the Michael Sobell Chemical Engineering Building

Light refreshments at *13:20*

Under the guidance of: *Prof. Yaron Paz*



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# "Enantioselective Photocatalysis - Design, Synthesis and Characterisation of a Composite Photocatalytic System for Chiral Separation"

Nitai Arbell

Supervisor: Prof. Yaron Paz

Despite the increasing demand for enantiopure compounds, currently available chiral purification technologies are still unable to fully meet market needs, due to throughput, complexity or operability considerations. We have developed a novel approach for the kinetic resolution of enantiomers, based on the selective adsorption of a target enantiomer onto a chirally imprinted surface of a photocatalyst, followed by its degradation via a photocatalytic mechanism. The approach is centred on a Photocatalytic Enantioenriching Device (PED) composed of a photocatalytic layer, on which the target enantiomer is adsorbed. A suppression layer of a photo-inert material is then grown around the adsorbed target molecules by Atomic Layer Deposition. After removal of the templating molecules, molecularly imprinted cavities with the same chirality as the adsorbed specie are obtained, allowing for the enantioselective degradation of the templated enantiomer through its enhanced adsorption, while dampening the non-selective degradation on the inert layer around the imprinted sites. The first model system tested was made using the dipeptide Leucylglycine as a model degradant,  $\text{TiO}_2$  as the photocatalytic material, and  $\text{Al}_2\text{O}_3$  as the inert overcoating layer, achieving a selectivity factor towards the degradation of the target enantiomer of up to seven, and an enrichment of up to 85% of a single enantiomer from an initially racemic mixture.

Additional work was performed on attempting to apply this method to the bismuth oxyhalide family of materials, which employ a direct-charge transfer photocatalytic mechanism, resulting in less non-selective degradation through the radically mediated mechanisms common in  $\text{TiO}_2$ . However, ALD-coating of these materials was found to be a challenge, due to their surface chemistry, resulting in the formulation of a UV-ozone surface treatment, which was found to significantly increase the conformality of the grown inert layers, and hence their activity-blocking capabilities. Experiments with visible-light photocatalysts were also carried out, in an attempt to expand the range of separable compounds to those which are UV-sensitive, degrading upon exposure to the UV light used to excite most photocatalysts. Some promising results were obtained, yet more work is required to properly utilise these materials.

Finally, as part of a joint project with another group member, the enantio-separation capabilities of  $\text{CePO}_4$ , a low-activity photocatalyst, were tested. Surprisingly,  $\text{CePO}_4$  was found to have inherent enantioselectivity when used with the amino acid Phenylalanine (PA), both as a photocatalyst, and as an adsorbing matrix, without the addition of any chirality-inducing modifications.  $\text{CePO}_4$  was able to completely purify an initially racemic mixture to 100% D-PA after 48 hours of adsorption, and enrich a racemic mixture to 90% D-PA after 150 hours of photocatalytic reaction. As  $\text{CePO}_4$  was also found to be capable of synthesising biomolecules such as nucleotides, this finding may even have importance for our understanding of the origin of life, and the homochirality of biological systems.