

### Epitaxial phases of high Bi content GaSbBi alloys

GaSbBi alloys have recently emerged as attractive materials for mid-infrared optoelectronics owing to strong band gap reduction enabled by Bi incorporation into the GaSb matrix. The fundamental understanding of the epitaxial process required to demonstrate high quality crystals is in an early-developmental phase. From this perspective, we report on the key role played by the Sb/Ga flux ratio in controlling the structural quality and incorporation of high Bi content GaSbBi (up to 14.5%-Bi), revealing three distinct epitaxial phases. The first phase (below stoichiometric Sb/Ga) exhibits Ga-Bi compound droplets, low crystal quality, and reduced Bi content. At the second phase (above stoichiometric Sb/Ga), the crystal exhibits smooth surfaces and excellent crystallinity with efficient Bi incorporation. The last phase corresponds to exceeding a Sb/Ga threshold that leads to reduced Bi incorporation, Bi droplets and degraded crystallinity. This threshold value that defines the optimal growth window is controlled by the temperature as well as the Bi/Ga ratio. Increasing temperature increases the threshold, albeit simultaneously reducing Bi incorporation. Conversely, increasing the Bi/Ga flux ratio increases Bi incorporation, while narrowing down and ultimately closing the window. This study provides a general framework enabling development of high quality GaSbBi heterostructures for emerging mid-infrared optoelectronics.

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Organisations: Physics, Research group: ORC

Contributors: Hilska, J., Koivusalo, E., Puustinen, J., Suomalainen, S., Guina, M.

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### Analysis of GaAsBi growth regimes in high resolution with respect to As/Ga ratio using stationary MBE growth

The control of Bi incorporation and material properties in III-V-Bi alloys has proved challenging due to their high sensitivity to the epitaxial growth parameters. Here, we present a methodology for determining the variation in the Ga, As, and Bi fluxes and the temperature across a stationary substrate in molecular beam epitaxy. By correlating the flux distributions with material properties, we identify distinct regimes for epitaxy of GaAsBi. In particular, we devise a detailed image of the interplay between Bi incorporation and structural properties of a bulk GaAs<sub>0.96</sub>Bi<sub>0.04</sub> layer grown on GaAs(1 0 0) with respect to the As/Ga ratio. The influence of As/Ga is analyzed with high resolution over the important stoichiometric range (i.e. As/Ga = 0.6–1.6). Growth outside the near-stoichiometric As/Ga regime leads to decreased Bi incorporation, decreased structural quality and the formation of Ga, Ga/Bi or Bi droplets. On the other hand, growth at As/Ga = 1.00–1.17 leads to maximized material quality. For this regime, the surface roughness is further optimized by fine-tuning the As/Ga ratio to suppress surface mounding to a value of 0.5 nm. The results reveal the extreme sensitivity of GaAsBi growth to small variations in the As/Ga ratio, and demonstrate the applicability of stationary growth in studying these effects.

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Research output: Contribution to journal > Article > Scientific > peer-review

### Reversible photodoping of TiO<sub>2</sub> nanoparticles

Observations on strong photochromic effect of crystalline TiO<sub>2</sub> quantum dots (mean size  $\approx$  4 nm) are presented. The synthesized quantum dots consist of irregularly shaped anatase TiO<sub>2</sub> nanoparticles (NPs) and are dispersed in butanol (8 % by mass). Obtained NPs exhibit a dramatic photo-response to UV light, enabling effective transmittance modulation of in a broad wavelength range extending from visible to near-infrared region, and even the thermal black body radiation regime beyond 10  $\mu$ m. The exceptional photo-response is attributed to hole-scavenging by butanol, TiO<sub>2</sub> self-reduction, injection of electrons to the conduction band, and consequent localized surface plasmon resonances in NPs. Observed optical effect is reversible and the initial high transmittance state can be restored simply by exposing the NPs to air. Applied NP synthesis route is economic and can be easily scaled for applications such as smart window technologies.

### General information

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Organisations: Photonics, Research group: Surface Science, Univ Tartu, University of Tartu, University of Tartu Institute of Physics, Inst Phys, University of Tartu

Contributors: Joost, U., Sutka, A., Oja, M., Smits, K., Doebelin, N., Loot, A., Järvekülg, M., Hirsimäki, M., Valden, M., Nommiste, E.

Pages: 8968-8974

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### Bibliographical note

INT=fot,"Joost, Urmas"

Research output: Contribution to journal > Article > Scientific > peer-review

## **Selenate removal in biofilm systems: Effect of nitrate and sulfate on selenium removal efficiency, biofilm structure and microbial community**

**BACKGROUND:** Selenium (Se) discharged into natural waterbodies can accumulate over time and have negative impacts on the environment. Se-laden wastewater streams can be treated using biological processes. However, the presence of other electron acceptors in wastewater, such as nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ), can influence selenate ( $\text{SeO}_4^{2-}$ ) reduction and impact the efficiency of biological treatment systems. **RESULTS:**  $\text{SeO}_4^{2-}$  removal by biofilms formed from an anaerobic sludge inoculum was investigated in the presence of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  using drip flow reactors operated continuously for 10 days at pH 7.0 and 30°C. The highest total Se (~60%) and  $\text{SeO}_4^{2-}$  (~80%) removal efficiencies were observed when the artificial wastewater contained  $\text{SO}_4^{2-}$ . A maximum amount of 68  $\mu\text{mol Se cm}^{-2}$  was recovered from the biofilm matrix in  $\text{SO}_4^{2-}$ + $\text{SeO}_4^{2-}$  exposed biofilms and biofilm mass was 2.7-fold increased for biofilms grown in the presence of  $\text{SO}_4^{2-}$ . When  $\text{SeO}_4^{2-}$  was the only electron acceptor, biofilms were thin and compact. In the simultaneous presence of  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$ , biofilms were thicker (> 0.6mm), less compact and exhibited gas pockets. **CONCLUSION:** The presence of  $\text{SO}_4^{2-}$  had a beneficial effect on biofilm growth and the  $\text{SeO}_4^{2-}$  removal efficiency, while the presence of  $\text{NO}_3^-$  did not have a significant effect on  $\text{SeO}_4^{2-}$  removal by the biofilms.

### **General information**

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Organisations: Chemistry and Bioengineering, Hydraulic and Environmental Engineering (IHE) Inst. for Water Education, Montana State University (MSU), Bhabha Atomic Research Centre, UPEM

Contributors: Tan, L. C., Espinosa-Ortiz, E. J., Nancharaiyah, Y. V., van Hullebusch, E. D., Gerlach, R., Lens, P. N.

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Original language: English

ASJC Scopus subject areas: Biotechnology, Chemical Engineering(all), Renewable Energy, Sustainability and the Environment, Fuel Technology, Waste Management and Disposal, Pollution, Organic Chemistry, Inorganic Chemistry

Keywords: Biofilm, Biofilm characterization, Co-electron acceptors, Nitrate, Selenate, Selenium removal, Sulfate

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## **Effect of surfactant type and sonication energy on the electrical conductivity properties of nanocellulose-CNT nanocomposite films**

We present a detailed study on the influence of sonication energy and surfactant type on the electrical conductivity of nanocellulose-carbon nanotube (NFC-CNT) nanocomposite films. The study was made using a minimum amount of processing steps, chemicals and materials, to optimize the conductivity properties of free-standing flexible nanocomposite films. In general, the NFC-CNT film preparation process is sensitive concerning the dispersing phase of CNTs into a solution with NFC. In our study, we used sonication to carry out the dispersing phase of processing in the presence of surfactant. In the final phase, the films were prepared from the dispersion using centrifugal cast molding. The solid films were analyzed regarding their electrical conductivity using a four-probe measuring technique. We also characterized how conductivity properties were enhanced when surfactant was removed from nanocomposite films; to our knowledge this has not been reported previously. The results of our study indicated that the optimization of the surfactant type clearly affected the formation of freestanding films. The effect of sonication energy was significant in terms of conductivity. Using a relatively low 16 wt. % concentration of multiwall carbon nanotubes we achieved the highest conductivity value of 8.4 S/cm for nanocellulose-CNT films ever published in the current literature. This was achieved by optimizing the surfactant type and sonication energy per dry mass. Additionally, to further increase the conductivity, we defined a preparation step to remove the used surfactant from the final nanocomposite structure.

### **General information**

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Materials Science, Faculty of Biomedical Sciences and Engineering, VTT Technical Research Centre of Finland

Contributors: Siljander, S., Keinänen, P., Rätty, A., Ramakrishnan, K. R., Tuukkanen, S., Kunnari, V., Harlin, A., Vuorinen, J., Kanerva, M.

Publication date: 20 Jun 2018

Peer-reviewed: Yes

#### Publication information

Journal: International Journal of Molecular Sciences

Volume: 19

Issue number: 6

Article number: 1819

ISSN (Print): 1661-6596

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Scopus rating (2018): CiteScore 5.2 SJR 1.312 SNIP 1.274

Original language: English

ASJC Scopus subject areas: Catalysis, Molecular Biology, Spectroscopy, Computer Science Applications, Physical and Theoretical Chemistry, Organic Chemistry, Inorganic Chemistry

Keywords: Carbon nanotubes, Conductivity, Nanocellulose, Nanocomposite, Surfactant

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#### Bibliographical note

INT=mol,"Rätty, Anna"

EXT="Harlin, Ali"

Source: Scopus

Source ID: 85048936349

Research output: Contribution to journal > Article > Scientific > peer-review

#### Photo-antimicrobial efficacy of zinc complexes of porphyrin and phthalocyanine activated by inexpensive consumer LED lamp

The properties and antimicrobial efficacies of zinc complexes of tetrakis(N-methylpyridinium-4-yl) tetraiodide porphyrin and tetrakis(N-methylpyridinium-4-yl) tetraiodide phthalocyanine impregnated to paper were evaluated. Photo-inactivation of microbes using inexpensive consumer light-emitting diode lamp was assessed on surface of dyed papers. Antimicrobial experiments of phthalocyanine-dyed paper by live cell assessment through colony forming units counting demonstrated 3.72 and 4.01 log reduction against *Escherichia coli* (*E. coli*) and *Acinetobacter baylyi* (*A. baylyi*) respectively after 1 h of illumination with 35 mW/cm<sup>2</sup> light. The porphyrin-dyed paper exhibited 1.66 and 2.01 log reduction in colony forming units against *E. coli* and *A. baylyi* respectively after 1 h exposure with 4 mW/cm<sup>2</sup> light. Both dyed papers were photo-stable after 64 h of continuous exposure with 42 mW/cm<sup>2</sup> light, while phthalocyanine-dyed paper exhibited superior leaching stability in phosphate-buffered saline.

#### General information

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Organisations: Chemistry and Bioengineering, Research group: Chemistry & Advanced Materials, Research group: Bio- and Circular Economy

Contributors: George, L., Hiltunen, A., Santala, V., Efimov, A.

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Original language: English

ASJC Scopus subject areas: Biochemistry, Inorganic Chemistry

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Research output: Contribution to journal › Article › Scientific › peer-review

### Thermal Isomerization of Hydroxyazobenzenes as a Platform for Vapor Sensing

Photoisomerization of azobenzene derivatives is a versatile tool for devising light-responsive materials for a broad range of applications in photonics, robotics, microfabrication, and biomaterials science. Some applications rely on fast isomerization kinetics, while for others, bistable azobenzenes are preferred. However, solid-state materials where the isomerization kinetics depends on the environmental conditions have been largely overlooked. Herein, an approach to utilize the environmental sensitivity of isomerization kinetics is developed. It is demonstrated that thin polymer films containing hydroxyazobenzenes offer a conceptually novel platform for sensing hydrogen-bonding vapors in the environment. The concept is based on accelerating the thermal cis-trans isomerization rate through hydrogen-bond-catalyzed changes in the thermal isomerization pathway, which allows for devising a relative humidity sensor with high sensitivity and quick response to relative humidity changes. The approach is also applicable for detecting other hydrogen-bonding vapors such as methanol and ethanol. Employing isomerization kinetics of azobenzenes for vapor sensing opens new intriguing possibilities for using azobenzene molecules in the future.

#### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Chemistry and Bioengineering, Aalto University

Contributors: Poutanen, M., Ahmed, Z., Rautkari, L., Ikkala, O., Priimägi, A.

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Research output: Contribution to journal › Article › Scientific › peer-review

### Gloriosa superba Mediated Synthesis of Platinum and Palladium Nanoparticles for Induction of Apoptosis in Breast Cancer

Green chemistry approaches for designing therapeutically significant nanomedicine have gained considerable attention in the past decade. Herein, we report for the first time on anticancer potential of phytogenic platinum nanoparticles (PtNPs) and palladium nanoparticles (PdNPs) using a medicinal plant *Gloriosa superba* tuber extract (GSTE). The synthesis of the nanoparticles was completed within 5 hours at 100°C which was confirmed by development of dark brown and black colour for PtNPs and PdNPs, respectively, along with enhancement of the peak intensity in the UV-visible spectra. High-resolution transmission electron microscopy (HRTEM) showed that the monodispersed spherical nanoparticles were within a size range below 10 nm. Energy dispersive spectra (EDS) confirmed the elemental composition, while dynamic light scattering (DLS) helped to evaluate the hydrodynamic size of the particles. Anticancer activity against MCF-7 (human breast adenocarcinoma) cell lines was evaluated using MTT assay, flow cytometry, and confocal microscopy. PtNPs and PdNPs showed 49.65 ± 1.99% and 36.26 ± 0.91% of anticancer activity. Induction of apoptosis was most predominant in the underlying mechanism which was rationalized by externalization of phosphatidyl serine and membrane blebbing. These findings support the efficiency of phytogenic fabrication of nanoscale platinum and palladium drugs for management and therapy against breast cancer.

#### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Faculty of Biomedical Sciences and Engineering, Modern College of Arts, Savitribai Phule Pune University, Indian Institute of Science, Bangalore, Department of Biomedical Sciences and Engineering, Defense Institute of Advanced Technology, Indian Institute of Technology Bombay, RK University

Contributors: Rokade, S. S., Joshi, K. A., Mahajan, K., Patil, S., Tomar, G., Dubal, D. S., Parihar, V. S., Kitture, R., Bellare, J. R., Ghosh, S.

Publication date: 2018

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Scopus rating (2018): CiteScore 2.6 SJR 0.383 SNIP 0.908

Original language: English

ASJC Scopus subject areas: Biochemistry, Organic Chemistry, Inorganic Chemistry

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Research output: Contribution to journal > Article > Scientific > peer-review

### Stable carbon isotopic composition of peat columns, subsoil and vegetation on natural and forestry-drained boreal peatlands

We studied natural and forestry-drained peatlands to examine the effect of over 34 years lowered water table on the  $\delta^{13}\text{C}$  values of vegetation, bulk peat and subsoil. In the seven studied sites,  $\delta^{13}\text{C}$  in the basal peat layer was 1.1 and 1.2 ‰ lower than that of the middle-layer and surface layer, respectively. Furthermore, there was a positive correlation between the  $\delta^{13}\text{C}$  values of the basal and surface peat layers, possibly due to carbon (C) recycling within the peat column. In the same mire complex, natural fen peat  $\delta^{13}\text{C}$  values were lower than those of the nearby bog, possibly due to the dominance of vascular plants on fen and the generally larger share of recycled C in the fens than in the bogs. Furthermore, natural and 51 years previously drained fen and bog, on the opposite sides of a ditch on the same mire complex, showed no significant differences in  $\delta^{13}\text{C}$  values. Plant  $\delta^{13}\text{C}$  values were lower, while  $\delta^{13}\text{C}$  values of subsoil were higher in the drained than in the natural site of the fen.

### General information

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MoE publication type: A1 Journal article-refereed

Organisations: Chemistry and Bioengineering, Research group: Bio- and Circular Economy, University of Eastern Finland, University of Jyväskylä

Contributors: Nykänen, H., Mpamah, P. A., Rissanen, A. J.

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Original language: English

ASJC Scopus subject areas: Environmental Chemistry, Environmental Science(all), Inorganic Chemistry

Keywords: Biogeochemistry, bog, carbon cycle, carbon dioxide, carbon-13, diagenesis, drainage, fen, isotope ecology, Sphagnum, Suess effect

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Research output: Contribution to journal > Article > Scientific > peer-review

### **Benchmarking DFT methods with small basis sets for the calculation of halogen-bond strengths**

In recent years, halogen bonding has become an important design tool in crystal engineering, supramolecular chemistry and biosciences. The fundamentals of halogen bonding have been studied extensively with high-accuracy computational methods. Due to its non-covalency, the use of triple-zeta (or larger) basis sets is often recommended when studying halogen bonding. However, in the large systems often encountered in supramolecular chemistry and biosciences, large basis sets can make the calculations far too slow. Therefore, small basis sets, which would combine high computational speed and high accuracy, are in great demand. This study focuses on comparing how well density functional theory (DFT) methods employing small, double-zeta basis sets can estimate halogen-bond strengths. Several methods with triple-zeta basis sets are included for comparison. Altogether, 46 DFT methods were tested using two data sets of 18 and 33 halogen-bonded complexes for which the complexation energies have been previously calculated with the high-accuracy CCSD(T)/CBS method. The DGDZVP basis set performed far better than other double-zeta basis sets, and it even outperformed the triple-zeta basis sets. Due to its small size, it is well-suited to studying halogen bonding in large systems.

### **General information**

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Organisations: Chemistry and Bioengineering, Research group: Supramolecular photochemistry

Contributors: Siiskonen, A., Priimägi, A.

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ISSN (Print): 1610-2940

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Scopus rating (2017): CiteScore 2.3 SJR 0.36 SNIP 0.534

Original language: English

ASJC Scopus subject areas: Catalysis, Computer Science Applications, Physical and Theoretical Chemistry, Organic Chemistry, Computational Theory and Mathematics, Inorganic Chemistry

Keywords: Basis set, Benchmarking, Density functional theory, Halogen bonding

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Research output: Contribution to journal > Article > Scientific > peer-review

### **Structurally Controlled Dynamics in Azobenzene-Based Supramolecular Self-Assemblies in Solid State**

Light-responsive supramolecular self-assemblies exhibit interplay between order and dynamics of the self-assembling motifs, through which the thermal isomerization rate of azobenzene chromophores can be tuned by orders of magnitude. By using supramolecular complexes of 4-(4-alkylphenylazo)phenols hydrogen-bonded to poly(4-vinylpyridine) as model systems, we demonstrate that the thermal isomerization rate of the hydroxyazobenzene derivatives increases 5700-fold when the material undergoes a transformation from a disordered, low-azobenzene-concentration state to a high-concentration state exhibiting lamellar, smectic-like self-assembly. Drastically smaller thermal isomerization rates are observed in disordered structures. This allows us to attribute the change to a combination of increased number density of the hydroxyazobenzenes inducing plasticization, and cooperativity created by the chromophore-chromophore interactions through self-assembled molecular order and alignment. Our results pinpoint the importance of molecular self-assembly and intermolecular interactions in modifying the dynamics in supramolecular complexes in a controlled manner. We foresee this to be important in light-controlled dynamic materials.

### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Department of Chemistry and Bioengineering, Research group: Supramolecular photochemistry, Aalto University

Contributors: Poutanen, M., Ikkala, O., Priimägi, A.

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Pages: 4095-4101

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Peer-reviewed: Yes

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Scopus rating (2016): CiteScore 9.8 SJR 2.564 SNIP 1.483

Original language: English

ASJC Scopus subject areas: Organic Chemistry, Materials Chemistry, Polymers and Plastics, Inorganic Chemistry

Electronic versions:

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Source: Scopus

Source ID: 84975044511

Research output: Contribution to journal > Article > Scientific > peer-review

### Synthesis, crystal structure, physico-chemical characterization and dielectric properties of a new hybrid material, 1-Ethylpiperazine-1,4-dium tetrachlorocadmate

### General information

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MoE publication type: A1 Journal article-refereed

Organisations: Department of Chemistry and Bioengineering, Carthage University, Laboratoire de chimie des Matériaux, Faculté des Sciences de Bizerte, Université de Carthage

Contributors: Dhieb, A. C., Valkonen, A., Rzaigui, M., Smirani, W.

Number of pages: 7

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Publication date: 15 Dec 2015

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### Publication information

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Volume: 1102

ISSN (Print): 0022-2860

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Scopus rating (2015): CiteScore 2.8 SJR 0.446 SNIP 0.837

Original language: English

ASJC Scopus subject areas: Spectroscopy, Analytical Chemistry, Inorganic Chemistry, Organic Chemistry

Keywords: Dielectric properties, IR-Raman spectroscopies, NMR spectroscopy, Phase transition, Photoluminescence, X-Ray diffraction

DOIs:

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Research output: Contribution to journal > Article > Scientific > peer-review



## Photomechanical Energy Transfer to Photopassive Polymers through Hydrogen and Halogen Bonds

The supramolecular assembly of photoactive azobenzenes with passive polymers via halogen or hydrogen bonding is a cost-effective way to design materials for various photomechanical applications that convert light energy directly into macroscopic motion, for instance, in all-optical surface patterning and photochemical imaging of plasmonic structures. To elucidate the molecular-level origins of this motion, we show, by coupling dynamic infrared spectroscopy to a photo-orientation setup, that supramolecular bonds above a certain interaction strength threshold are photostable under vigorous photoisomerization cycling and capable of translating the photo-orientation of azobenzenes into the orientation of nonabsorbing host polymer side chains. A correlation is found between azobenzene photoinduced molecular orientation and macroscopic all-optical surface patterning efficiency. The improved performance of halogen-bonded systems in photopatterning applications can be related to the absence of a plasticizing effect on the polymer matrix, which may enable the material to retain an optimal glass transition temperature, in contrast to hydrogen-bonded and nonbonded references. Thus, our results provide design guidelines in terms of the nature and strength of the supramolecular interaction and of the degree of azo functionalization needed to optimize the motion transfer to passive polymers.

### General information

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Organisations: Department of Chemistry and Bioengineering, Research group: Supramolecular photochemistry, Frontier Photonics, Département de Chimie, Succ. Centre-Ville, Aalto University, Politecnico di Milano, Royal Military College of Canada

Contributors: Vapaavuori, J., Heikkinen, I. T. S., Dichiarante, V., Resnati, G., Metrangolo, P., Sabat, R. G., Bazuin, C. G., Priimagi, A., Pellerin, C.

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Peer-reviewed: Yes

### Publication information

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ISSN (Print): 0024-9297

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Original language: English

ASJC Scopus subject areas: Organic Chemistry, Materials Chemistry, Polymers and Plastics, Inorganic Chemistry

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### Bibliographical note

EXT="Vapaavuori, Jaana"

Source: Scopus

Source ID: 84945400553

Research output: Contribution to journal > Article > Scientific > peer-review

## In Situ Photocontrol of Block Copolymer Morphology during Dip-Coating of Thin Films

We demonstrate a unique combination of simultaneous top-down and bottom-up control of the morphology of block copolymer films by application of in situ optical irradiation during dip-coating. A light-addressable and block-selective small molecule, 4-butyl-4'-hydroxyazobenzene (BHAB), is introduced into a diblock copolymer of polystyrene and poly(4-vinylpyridine) (PS-P4VP) of 28.4 wt % P4VP via supramolecular chemistry, notably by hydrogen bonding to P4VP. We show that the spherical morphology of thin films dip-coated from a THF solution at slow withdrawal rates in the dark convert to cylindrical morphology when dip-coated under illumination. This is attributed to volume expansion of the P4VP/BHAB phase due to trans-cis photoisomerization combined with a light-induced increase in BHAB uptake in the film. The demonstrated photocontrol highlights the potential of dip-coating as a scalable film preparation method that can be easily coupled with external stimuli to direct nanostructured self-assembly in the films as solvent evaporates.

### General information

Publication status: Published  
MoE publication type: A1 Journal article-refereed  
Organisations: Frontier Photonics, Département de Chimie, Succ. Centre-Ville  
Contributors: Vapaavuori, J., Grosrenaud, J., Pellerin, C., Bazuin, C. G.  
Number of pages: 5  
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Publication date: 20 Oct 2015  
Peer-reviewed: Yes

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Scopus rating (2015): CiteScore 10.1 SJR 2.392 SNIP 1.403

Original language: English

ASJC Scopus subject areas: Organic Chemistry, Materials Chemistry, Polymers and Plastics, Inorganic Chemistry

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Source: Scopus

Source ID: 84946032702

Research output: Contribution to journal > Article > Scientific > peer-review

#### Unintentional boron contamination of MBE-grown GaInP/AlGaInP quantum wells

The effects of unintentional boron contamination on optical properties of GaInP/AlGaInP quantum well structures grown by molecular beam epitaxy (MBE) are reported. Photoluminescence and secondary-ion mass spectrometry (SIMS) measurements revealed that the optical activity of boron-contaminated quantum wells is heavily affected by the amount of boron in GaInP/AlGaInP heterostructures. The boron concentration was found to increase when cracking temperature of the phosphorus source was increased. Boron incorporation was enhanced also when aluminum was present in the material.

#### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Optoelectronics Research Centre, Research group: Semiconductor Technology and Applications, Frontier Photonics, VTT Technical Research Centre of Finland

Contributors: Tukiainen, A., Likonen, J., Toikkanen, L., Leinonen, T.

Pages: 60-63

Publication date: 1 Sep 2015

Peer-reviewed: Yes

#### Publication information

Journal: Journal of Crystal Growth

Volume: 425

ISSN (Print): 0022-0248

Ratings:

Scopus rating (2015): CiteScore 3.3 SJR 0.686 SNIP 1.066

Original language: English

ASJC Scopus subject areas: Condensed Matter Physics, Materials Chemistry, Inorganic Chemistry

Keywords: A1. Defects, A1. Impurities, A3. Molecular beam epitaxy, B1. Phosphides, B2. Semiconducting III-V materials

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Source ID: 84951561374

Research output: Contribution to journal > Article > Scientific > peer-review

#### Synthesis, characterization and solid-state photoluminescence studies of six alkoxy phenylene ethynylene dinuclear palladium(ii) rods

A rare family of six discrete binuclear  $[\text{PdCl}(\text{PEt}_3)_2]$  phenylene ethynylene rods with alkoxy side chains (methoxy, ethoxy and heptoxy) have been developed, and their solid-state photoluminescence results have been presented and discussed. The shorter bridging ligands are of the general formula  $\text{H}-\text{CC}-\text{C}_6\text{H}_2(\text{R})_2-\text{CC}-\text{H}$ , where  $\text{R} = \text{H}, \text{OCH}_3, \text{OC}_2\text{H}_5,$  and  $\text{OC}_7\text{H}_{15}$ , whereas the longer ones are based on  $\text{H}-\text{CC}-\text{C}_6\text{H}_4-\text{CC}-\text{C}_6\text{H}_2(\text{R})_2-\text{CC}-\text{C}_6\text{H}_4-\text{CC}-\text{H}$ , where  $\text{R} = \text{OCH}_3, \text{OC}_2\text{H}_5$ . These ligands display increasing length in both the main dimension (backbone length) as well as the number of carbons in the side chains ( $\text{R}$ , alkoxy side chain) that stem from the central phenylene moiety. The X-ray crystal structures of two of the prepared complexes are reported: one corresponds to a shorter rod, 1,4-bis[trans-( $\text{PEt}_3$ ) $_2$ ClPd-CC]-2,5-diethoxybenzene (6c), while the second one is associated with a longer rod, the binuclear complex 1,4-bis[trans-( $\text{PEt}_3$ ) $_2$ ClPd-4-(-CC-C $_6$ H $_4$ -CC)]-2,5-diethoxybenzene (7c). All new compounds were characterized by NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$ ) as well as ESI-MS(TOF), EA, FTIR, UV-Vis, cyclic voltammetry and solid-state photoluminescence. Our work shows the influence of the alkoxy side chains on the electronic structure of the family of binuclear Pd rods by lowering its oxidation potential. In addition to this, the increase of the length of the bridge results in a higher oxidation potential. Solid state photoluminescence results indicate that Pd complexes are characterized by a marked decrease in both the emission intensity and the fluorescence lifetime values as compared to their ligands. This behaviour could be due to some degree of ligand-to-metal charge transfer. This journal is

### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: University of Jyväskylä, CQM-Centro de Química da Madeira, Universidade da Madeira Campus Universitário da Penteada, MMRG, Departamento de Física Fundamental y Experimental, Facultad de Física, Universidad de la Laguna

Contributors: Figueira, J., Czardybon, W., Mesquita, J. C., Rodrigues, J., Lahoz, F., Russo, L., Valkonen, A., Rissanen, K.

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Publication date: 7 Mar 2015

Peer-reviewed: Yes

### Publication information

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Original language: English

ASJC Scopus subject areas: Inorganic Chemistry

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Research output: Contribution to journal > Article > Scientific > peer-review

### Polymer looping is controlled by macromolecular crowding, spatial confinement, and chain stiffness

We study by extensive computer simulations the looping characteristics of linear polymers with varying persistence length inside a spherical cavity in the presence of macromolecular crowding. For stiff chains, the looping probability and looping time reveal wildly oscillating patterns as functions of the chain length. The effects of crowding differ dramatically for flexible versus stiff polymers. While for flexible chains the looping kinetics is slowed down by the crowdors, for stiffer chains the kinetics turns out to be either decreased or facilitated, depending on the polymer length. For severe confinement, the looping kinetics may become strongly facilitated by crowding. Our findings are of broad impact for DNA looping in the crowded and compartmentalized interior of living biological cells.

### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Department of Physics, Institute for Physics and Astronomy, University of Potsdam, Max-Planck Institute for the Physics of Complex Systems

Contributors: Shin, J., Cherstvy, A. G., Metzler, R.

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Pages: 202-206

Publication date: 17 Feb 2015

Peer-reviewed: Yes

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Original language: English

ASJC Scopus subject areas: Organic Chemistry, Materials Chemistry, Polymers and Plastics, Inorganic Chemistry

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Source ID: 84923204435

Research output: Contribution to journal › Article › Scientific › peer-review

### A supramolecular approach to photoresponsive thermo/solvoplastic block copolymer elastomers

With the aim of preparing supramolecular photoresponsive block copolymer elastomers, a series of ABA triblock copolymers with a poly(*n*-butyl acrylate) (PnBA) middle block and poly(dimethylaminoethyl methacrylate) (PDMAEMA or PDM) outer blocks were synthesized by atom transfer radical polymerization (ATRP), followed by PDM quaternization (giving PDMQ-PnBA-PDMQ) and then by ionic complexation with methyl orange (MO), an azo-containing and sulfonate-functionalized commercially available compound (giving PDMQ/MO-PnBA-PDMQ/MO). The PnBA block, which has a subambient glass transition, and the quaternized and complexed blocks, which have high glass transitions, form phase-separated soft and hard blocks, respectively. Simple elasticity tests of solvent-cast films show that the PDMQ/MO-PnBA-PDMQ/MO with hard block content between 18 and 29 wt % (as well as PDMQ-PnBA-PDMQ with 18 wt % hard block content) have significant elastomeric character. AFM and TEM (atomic force and transmission electron microscopies) of spin-coated films show a correlation between the elastomeric character and morphologies where the hard block forms a dispersed minority phase (spherical and/or short cylindrical domains). A continuous hard phase is observed for a hard block content of around 37 wt %; these materials show no significant elasticity. Reversible photoisomerization, with relatively high *cis* isomer content in the photostationary state, was also demonstrated.

### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Department of Computer Systems, Frontier Photonics, Département de Chimie, Succ. Centre-Ville, Université de Sherbrooke

Contributors: Wang, X., Vapaavuori, J., Zhao, Y., Bazuin, C. G.

Number of pages: 10

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Original language: English

ASJC Scopus subject areas: Organic Chemistry, Materials Chemistry, Polymers and Plastics, Inorganic Chemistry

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Research output: Contribution to journal › Article › Scientific › peer-review

### Zinc coordination spheres in protein structures

Zinc metalloproteins are one of the most abundant and structurally diverse proteins in nature. In these proteins, the Zn(II) ion possesses a multifunctional role as it stabilizes the fold of small zinc fingers, catalyzes essential reactions in enzymes of all six classes, or assists in the formation of biological oligomers. Previously, a number of database surveys have been

conducted on zinc proteins to gain broader insights into their rich coordination chemistry. However, many of these surveys suffer from severe flaws and misinterpretations or are otherwise limited. To provide a more comprehensive, up-to-date picture on zinc coordination environments in proteins, zinc containing protein structures deposited in the Protein Data Bank (PDB) were analyzed in detail. A statistical analysis in terms of zinc coordinating amino acids, metal-to-ligand bond lengths, coordination number, and structural classification was performed, revealing coordination spheres from classical tetrahedral cysteine/histidine binding sites to more complex binuclear sites with carboxylated lysine residues. According to the results, coordination spheres of hundreds of crystal structures in the PDB could be misinterpreted due to symmetry-related molecules or missing electron densities for ligands. The analysis also revealed increasing average metal-to-ligand bond length as a function of crystallographic resolution, which should be taken into account when interrogating metal ion binding sites. Moreover, one-third of the zinc ions present in crystal structures are artifacts, merely aiding crystal formation and packing with no biological significance. Our analysis provides solid evidence that a minimal stable zinc coordination sphere is made up by four ligands and adopts a tetrahedral coordination geometry.

#### General information

Publication status: Published

MoE publication type: A1 Journal article-refereed

Organisations: Multi-scaled biodata analysis and modelling (MultiBAM), Ita-Suomen yliopisto, School of Management (JKK)

Contributors: Laitaoja, M., Valjakka, J., Jänis, J.

Number of pages: 9

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Peer-reviewed: Yes

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Original language: English

ASJC Scopus subject areas: Inorganic Chemistry, Physical and Theoretical Chemistry

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Source: Scopus

Source ID: 84885131955

Research output: Contribution to journal › Article › Scientific › peer-review

#### Location of the Azobenzene moieties within the cross-linked liquid-crystalline polymers can dictate the direction of photoinduced bending

We present a simple way to control the photoinduced bending direction of azobenzene-containing cross-linked liquidcrystalline polymers. By changing the location of the photoactive azobenzene moieties from cross-links to side-chains, the bending direction of the sample is reversed under identical irradiation conditions. In addition to providing a versatile route toward directionality control of the photoinduced macroscopic motions, this observation highlights the complicated nature of the photomechanical response of azobenzene-containing cross-linked liquidcrystalline polymers, showing that the photomobile behavior can be determined by seemingly small details on the materials design.

#### General information

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MoE publication type: A1 Journal article-refereed

Organisations: Frontier Photonics, Aalto University, Tokyo Institute of Technology, University of Hyogo, Kobe, Tohoku University, Chuo University

Contributors: Primagi, A., Shimamura, A., Kondo, M., Hiraoka, T., Kubo, S., Mamiya, J. I., Kinoshita, M., Ikeda, T., Shishido, A.

Number of pages: 4

Pages: 96-99

Publication date: 2012

Peer-reviewed: Yes

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Original language: English

ASJC Scopus subject areas: Organic Chemistry, Materials Chemistry, Polymers and Plastics, Inorganic Chemistry  
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Source: Scopus

Source ID: 84861898337

Research output: Contribution to journal > Article > Scientific > peer-review

### Electronic and structural properties of Si<sub>10</sub> cluster

Possible structures for Si<sub>10</sub> cluster are considered using a tight-binding model and drawing on significant work done in the past. It is shown that the tight-binding parametrization, fitted to the bulk, is also valid for smaller systems. This model is found to essentially reproduce other published results, but requires much less effort than ab initio techniques—thus, allowing the study of a wide variety of structures and their ions. However, unlike classical force-field calculations, it yields information about the electronic structure of clusters. A new geometric structure for Si<sub>10</sub> is found, which is not only of lowest energy, but which also matches the experimental photoelectron band gap and explains the experimental reactivity data. Because of the Jahn-Teller effect, the photoelectron spectrum is very sensitive to geometry. Also, ionization of the cluster alters the geometry slightly.

### General information

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MoE publication type: A1 Journal article-refereed

Organisations: Departments of Chemistry, and Physics and Astronomy, 239 Fronczak Hall, State University of New York, College at Fredonia

Contributors: Rantala, T. T., Jelski, D. A., George, T. F.

Number of pages: 12

Pages: 189-200

Publication date: Jun 1990

Peer-reviewed: Yes

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Issue number: 2

ISSN (Print): 1040-7278

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ASJC Scopus subject areas: Inorganic Chemistry

Keywords: Silicon clusters, tight-binding model

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