

TGSW2016  
Session 7: Green Innovation  
19<sup>th</sup> September @ room 402

	<b>Energy Materials</b>	Chair: Hideharu Niwa (UT)
13:30 - 14:00 (invited)	<b>Ching-Shun Ku and Di-Jing Huang (NSRRC, Taiwan)</b> Opportunities of Taiwan Photon Source for Energy Material Research	
14:00 – 14:20	<b>Venkatesha Rama Hathwar</b> , Eiji Nishibori, Bo Iversen, Yutaka Moritomo (UT) Is the crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ so simple to understand?	
14:20 – 14:50 (invited)	<b>Pirmin Ulmann (IMERYS Graphite &amp; Carbon, Switzerland)</b> Carbon-based Negative Electrode Active Materials for Lithium-ion Batteries –Past, Present and Trends towards the Future	
14:50 – 15:10	break	
	<b>Polymer Materials</b>	Chair: Yohei Yamamoto (UT)
15:10- 15:30	<b>Takaki Kanbara (UT)</b> Synthesis of fluorene-based conjugated polymers via direct arylation polycondensation	
15:30 – 16:00 (invited)	<b>Xike Gao (Shanghai Institute of Organic Chemistry, China)</b> Conjugated Diimides for Organic Optoelectronic Materials: Molecular Design and Synthesis	
16:00 – 16:30 (invited)	<b>Weishi Li (Shanghai Institute of Organic Chemistry, China)</b> Poly(rod-coil) Polymeric Semiconductors: a new class of Organic Optoelectronic Materials	
18:00 – 20:00	<b>Banquet</b>	

# Opportunities of Taiwan Photon Source for Energy Material Research

*Ching-Shun Ku and Di-Jing Huang*

*National Synchrotron Radiation Research Center (NSRRC), Hsinchu, TAIWAN*

Recently the National Synchrotron Radiation Research Center (NSRRC) in Taiwan has successfully constructed a low-emittance 3 GeV synchrotron light source, the Taiwan Photon Source (TPS). The TPS with a circumference of 518 m is composed of 24 double-bend achromatic (DBA) cells connected by six 12-m straight sections and eighteen 7-m straight sections. The natural emittance of the TPS is 1.6 nm · rad with a small dispersion in the straight sections. Figure 1 displays an aerial photograph of the NSRRC. The TPS commissioning proceeded at a speedy pace, delivering its first synchrotron light in December 2014 and the electron current in the storage ring reaching 100 mA in March 2015. In phase-I operation, the TPS uses two sets of KEK-B type superconducting RF cavities to achieve an electron current of 500 mA in a top-up injection mode.

Taking full advantage of the high-brilliance of TPS, the phase-I beamlines aim for the forefront of research to cover the diverse photon sciences in an energy range from soft to hard X-rays. These beamlines are optimized for protein micro-crystallography, low-energy excitations of novel materials with atomic specificity, spectroscopy and diffraction on the submicron and nanometer scales, scattering of coherent X-rays, and scanning nanoprobe studies that will resolve structures in a spatial resolution of tens nm. Currently four of the TPS phase-I beamlines are available to users; other three beamlines are scheduled to deliver photons in 2017.

In this talk, we will present the specifications and commissioning results of the TPS phase-I beamlines for energy material research. In particular, we will discuss the opportunities of using high-resolution X-ray powder diffraction, X-ray nanodiffraction and coherent diffraction including ptychography, followed by an overview of future beamline plan.



Figure 1: An aerial photograph of the NSRRC. This photograph shows the recently completed TPS and the 21-year-old Taiwan Light Source (TLS). The proposal of the TPS project was prepared in 2004. The civil construction of the TPS began in February 2010, and was completed in December 2013. The assembly of main accelerator parts was completed in 2014. The TPS project came to realization after ten years of efforts.

## Is the crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ so simple to understand?

Venkatesha R. Hathwar,<sup>a</sup> Eiji Nishibori,<sup>a</sup> Bo B. Iversen,<sup>b</sup> Yutaka Moritomo<sup>a</sup>

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The hybrid inorganic–organic perovskite,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  has become very promising candidate for photovoltaic applications due to its high solar cell efficiency, even exceeding 20%.<sup>1</sup> The possibility of easy processing and solution based low cost synthesis make it an attractive alternative to silicon based devices. Beside these continuous effort on device improvements, an ambiguity about the crystal structure of tetragonal phase of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is still not clear. The tetragonal crystal structure is reported in both polar and non-polar space groups,<sup>2</sup> where respective claims were further supported by P-E loop measurements and SHG efficiency. Recently, a piezoelectric force microscopy (PFM) experiments show ferroelectric nano-domains in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin films.<sup>3</sup> In order to resolve the crystal structure contradictions, we have collected high resolution synchrotron X-ray data at SPring-8 on single crystals ( $< 50 \mu\text{m}^3$ ) and the crystal structures are solved in both polar and non-polar space groups. Measured synchrotron X-ray data and obtained crystallographic results indicate a non-polar crystal structure for  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , which seems to be preferable around room temperature with a coexistence of inversion twinning of micro-domains in the crystal. In my presentation, I will discuss our results in the context of sample size, quality of X-ray data and observation of twinning.

### References:

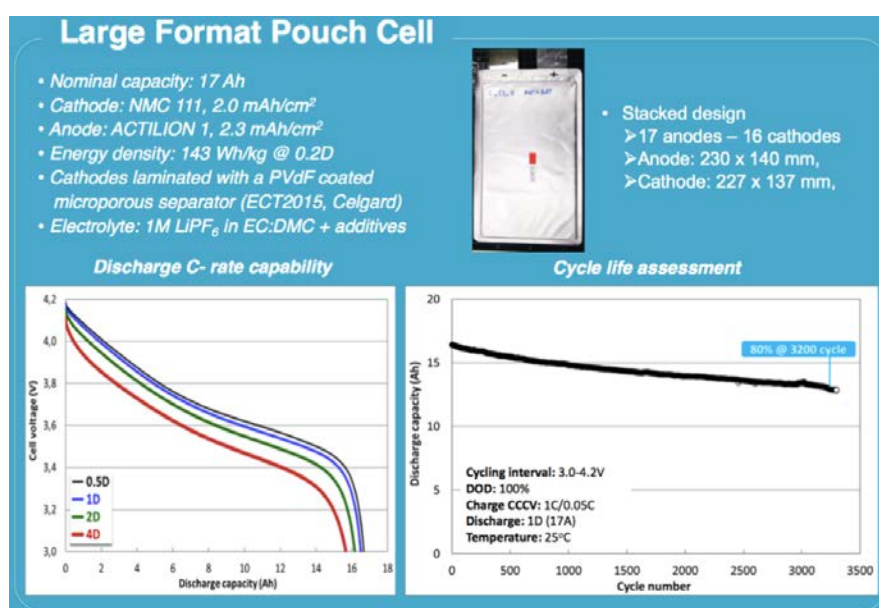
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# Carbon-Based Negative Electrode Active Materials for Lithium-Ion Batteries – Past, Present and Trends towards the Future

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Starting with a comparison of electrochemical characteristics exhibited by different types of carbon that have historically been used as negative electrode materials in lithium-ion batteries (coke, hard & soft carbon, synthetic & natural graphite),<sup>1</sup> recent large format pouch cell results obtained based on a hydrophilic graphite active material and water-processed electrodes will be presented (see Figure).<sup>2</sup> Examples of Si, Sn and alloy-based active materials which are typically used in combination with conductive carbons will be discussed as well.

Finally, some general considerations will be made as to how ‘frictions’ that slow down development efforts made by lithium-ion battery researchers could potentially be



reduced by the use of ‘open innovation’<sup>3</sup> and ‘open-source’<sup>4</sup> concepts.

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# Synthesis of fluorene-based conjugated polymers via direct arylation polycondensation

Takaki Kanbara

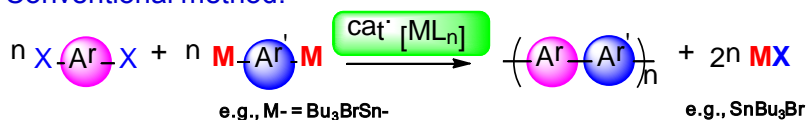
Tsukuba Research Center for Interdisciplinary Materials Science (TIMS),  
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Catalytic direct arylation of aromatic compounds via cleavage of C-H bonds of aromatic compounds and the dehydrohalogenative cross-coupling reaction has attracted increasing attention as a simple synthetic method because it allows for elimination of the use of organometallic reagents and reducing undesired waste originating from the organometallic reagents. Recently, several groups have attempted to utilize this reaction in polycondensation for the synthesis of  $\pi$ -conjugated polymers. We have envisioned development of the direct arylation polycondensation as a general and reliable method; expansion of this synthetic protocol allows for the polycondensation of various aromatic monomers. This atom- and step-economical protocol also lends itself to practical application for fabrication of organic devices such as organic photovoltaics cells, field effect transistors, and light emitting diodes.

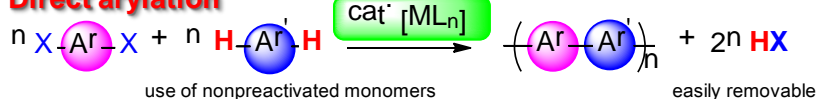
Firstly, we have focused on exploring the targeting aromatic monomers including the highly active C-H bond for the metal-catalyzed functionalization. On the other hand, with respect to the coupling partner, 2,7-dibromo-9,9-dialkylfluorene is an appropriate monomer because it possesses good reactivity toward the direct arylation polycondensation and high selectivity against side reaction. Consequently, the appropriate choices of monomers and detailed optimization of the reaction conditions provided a variety of fluorene-based  $\pi$ -conjugated polymers via the direct arylation polycondensation.

In this presentation, our recent activities on the facile synthetic protocol will also be presented.

Conventional method:



Direct arylation



# Conjugated Diimides for Organic Optoelectronic Materials: Molecular Design and Synthesis

Xike Gao

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Organic thin film transistors (OTFTs) and organic photovoltaics (OPVs) have attracted ever increasing attention due to their applications in low-cost, large-area, and flexible semiconducting devices. In the field of OTFTs and OPVs, the n-type (electron-transporting) organic semiconductors (OSCs) are outmatched by their burgeoning p-type (hole-transporting) counterparts [1]. Excellent n-type OSCs are highly necessary for constructing low-power-consumption organic complementary circuits and bulk-heterojunction OPVs with the p-type ones. In the past six years, we developed a class of core-expanded naphthalene diimides (NDI), named as NDI-DTYM2, and their-based solution-processed n-channel OTFTs showed high electron mobility ( $0.1\text{--}3.5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ) and excellent device stability in air [2]. In addition, NDI fused with two 2-(1,3-dithiol-2-ylidene)acetonitrile moieties (NDI-DTYA2), a novel strong electron-deficient monomer, was designed and synthesized to develop n-type polymers [3]. Recently, we created a novel class of azulene-based conjugated diimides, 2,2'-biazulene-1,1',3,3'-tetracarboxylic diimides (BAZDIs), which have unique photophysical properties and are promising for organic optoelectronic materials [4].

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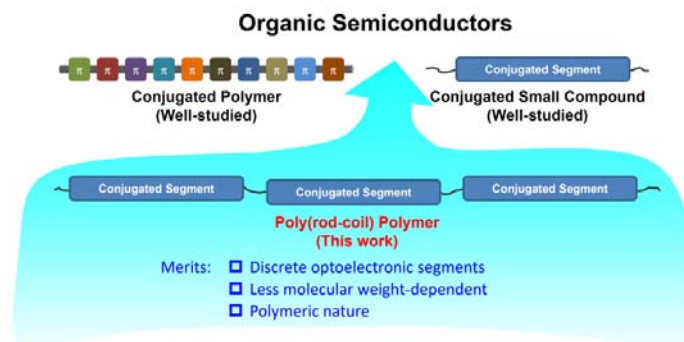
# Poly(rod-coil) Polymeric Semiconductors: a new class of Organic Optoelectronic Materials

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Owing to their features of light weight, flexibility, low cost, solution-processibility, and adaptability for large area device fabrication, organic electronics has attracted considerable attention from both scientific and industrial communities. With tremendous effort in material innovation in the past decades, a huge number of organic semiconductors have been developed, some of which showed high performance in photovoltaics, light-emitting diodes, and/or field-effect transistors. Although their chemical structures are in a wide diversity, most of them can be categorized into two classes: conjugated polymers and small molecular compounds. In general, conjugated polymers have a good film-formation potential due to their polymeric nature. Moreover, conjugated polymers possess one-dimensional extended  $\pi$ -conjugated backbones, which are favorable to transduction of charge carriers and excitons and benefit their optoelectronic performances. However, they are always the mixtures of homologues having different lengths of conjugated backbones. It has been well documented that molecular weight and its polydispersity have significant influence on optoelectronic performance of conjugated polymers. This causes a severe problem for their real use: poor batch reproducibility. In contrary, small molecular semiconductors do not have such batch-dependent problem because of their definite chemical structures. However, for achieving efficient light absorption and good charge transportation among molecules, this kind of materials usually have a large and rigid  $\pi$ -conjugated core. As a result, they tend to aggregate or crystallize in film state and are hard to form a well-qualified homogenous film, particularly in a large size.

Recently, we proposed a new type of organic semiconductors, which is a kind of poly(rod-coil) polymers alternatively composed of definite conjugated and non-conjugated segments (Fig. 1).<sup>1-3</sup> The conjugated segments are optoelectronically active and have a fixed chemical structure, like small molecular semiconductors. Thus, it could be expected to have less molecular weight-dependent optoelectronic properties. Moreover, their polymeric nature may endow them a good film formation behavior. In this presentation, I will report several examples of this type of organic semiconductors and their applications in organic solar cells and field-effect transistors.



**Fig. 1** Schematic representation of proposed poly(rod-coil) organic semiconductors

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