

Academic Program [Oral B] | 04. Physical Chemistry -Properties- : Oral B

📅 Thu. Mar 27, 2025 3:55 PM - 4:55 PM JST | Thu. Mar 27, 2025 6:55 AM - 7:55 AM UTC 🏛️
[C]C303(C303, Bldg. 2, Area 2 [3F])

[[C]C303-2vn] 04. Physical Chemistry -Properties-

Chair: Takuya Okamoto, Kenta Nakagawa

📌 English

3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC

[[C]C303-2vn-01]

Growth of thalidomide single crystals using sublimation method and evaluation of the racemization

○ Mizuki Kira¹, Yuta Shiga¹, Kenta Nakagawa², Ayaka Matsumoto¹, Keigo Tokita¹, Yukana Terasawa³, Kun Zhang¹, Koichi Tsutao¹, Takuya Nakanishi², Satoshi Yoshida⁴, Sota Sato⁴, Norio Shibata⁵, Toru Asahi^{1,2} (1. Faculty of Adv. Sci. & Eng., Waseda Univ., 2. Comprehensive Research Org., Waseda Univ., 3. Faculty of Eng., Kumamoto Univ., 4. Faculty of Eng., the Univ. of Tokyo, 5. Nagoya Inst. of Tech.)

📌 English

4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC

[[C]C303-2vn-02]

Synthesis of Titanium Nitride Semiconductor Nanocrystals

○ Aswathi Maladan¹, Takuya Okamoto¹, Biju Vasudevanpillai¹, Subrahmanyam Challapalli², Most Farida Khatun¹, Mohit Kumar² (1. Hokkaido University, 2. IIT Hyderabad)

📌 English

4:35 PM - 4:55 PM JST | 7:35 AM - 7:55 AM UTC

[[C]C303-2vn-03]

Synthesis and study of NHC functionalized diarylethene ligand for photoswitchable catalysis

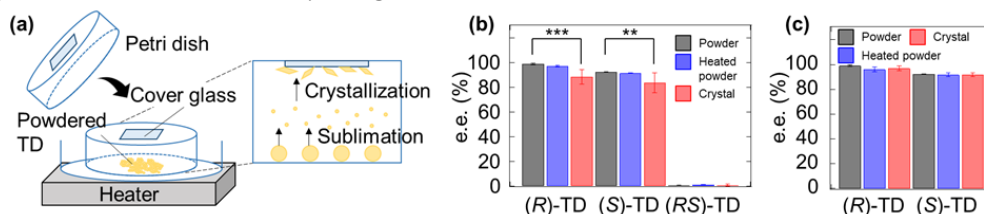
○ Marine Louis¹, Taihei Kanou², Makoto Machiyama³, Seiji Mori³, Tsuyoshi Kawai², Lucie Jarrige⁴ (1. Tokyo University of Agriculture and Technology, 2. Nara Institute of Science and Technology, 3. Ibaraki University, 4. Rennes Institute of Chemical Science)

昇華法を用いたサリドマイド単結晶成長およびラセミ化の検証

(早大院先進理工¹・早大総研機構²・熊大院工³・東大工⁴・名工大工⁵)
 ○吉良美月¹・志賀勇太¹・中川鉄馬²・松本綾香¹・時田桂吾¹・寺澤有果菜³・チヨウコン¹・蔦尾滉一¹・中西卓也²・吉田知史⁴・佐藤宗太⁴・柴田哲男⁵・朝日透^{1,2}
 Growth of thalidomide single crystals using sublimation method and evaluation of racemization (¹Faculty of Adv. Sci. & Eng., Waseda Univ., ²Comp. Res. Org., Waseda Univ., ³Faculty of Eng., Kumamoto Univ., ⁴Faculty of Eng., the Univ. of Tokyo, ⁵Dept. of Eng., Nagoya Inst. of Tech.) ○Mizuki Kira¹, Yuta Shiga¹, Kenta Nakagawa², Ayaka Matsumoto¹, Keigo Tokita¹, Yukana Terasawa³, Kun Zhang¹, Koichi Tsutao¹, Takuya Nakanishi², Satoshi Yoshida⁴, Sota Sato⁴, Norio Shibata⁵, Toru Asahi^{1,2}

3'-(*N*-phthalimido)glutarimide, commonly named thalidomide (TD), is one of the most famous chiral drugs, and its serious side effect caused by the teratogenicity of the (*S*)-enantiomer only has led to drug-related incidents.¹⁾ To understand the pharmacodynamics and pharmacokinetics of TD, it is useful to understand its physicochemical properties not only in solution but also in solid state.^{2,3)} Therefore, in this study, we examined the process of crystal growth of solid-state TDs. We grew single crystals of (*R*)-, (*S*)-, and (*RS*)-TD using the sublimation method, and confirmed that the sublimation method is effective for growing TD crystals through Raman spectroscopy and single crystal X-ray structure analysis⁴⁾. The change in enantiomeric excess (e.e.) during crystal growth was also investigated by HPLC analysis, which revealed that TD undergoes chiral inversion during sublimation under normal laboratory conditions. On the other hand, chiral inversion was not observed under low humidity conditions, and this suggests that the interaction with water vapor in the air is a cause of this phenomenon. This is an important finding to prevent undesirable effects in the purification of chiral drugs using sublimation.

Keywords : Thalidomide; Crystal growth; Chiral inversion; Sublimation



本図は American Chemical Society から承諾を得て転載

3'-(*N*-フタルイミド)グルタルイミド、通称サリドマイド (TD) は、最も有名なキラル医薬品の一つであり、(*S*) 体のエナンチオマーのみが示す催奇形性によって生じた重篤な副作用が薬害事件を引き起こした¹⁾。TD の薬力学・薬物動態を理解するためには、溶液状態だけでなく固相状態での物理化学的性質も有用である^{2,3)}。よって本研究では、固体 TD の結晶育成の過程について、検証を行った。昇華法を用いて (*R*)-、(*S*)-、(*RS*)-TD の単結晶を育成し、ラマン分光法や単結晶 X 線構造解析を通じて、昇華法が TD 結晶の成長に有効であることを確認した⁴⁾。また、HPLC 解析により結晶育成中のエナンチオマー過剰率 (e.e.) の変化を調べた結果、通常の実験室環境下では昇華中に TD がキラル反転を起こすことが明らかになった。一方、低湿度環境下ではキラル反転は観察されず、空気中の水蒸気との相互作用がこの現象の原因であることが示唆された。この結果は、昇華を利用したキラル薬物の精製において、望ましくない効果を防ぐために重要な知見である。

1) G. Blaschke, *et al.*, *Arzneimittel-Forschung* **1979**, 29, 1640-1642. 2) B. Knoche, *et al.*, *J. Chromatogr. A*, **1994**, 666, 235-240. 3) K. Nishimura, *et al.*, *Chem. Pharm. Bull.*, **1994**, 42, 1157-1159. 4) E. Tokunaga, *et al.*, *Sci. Rep.*, **2018**, 8, 17131. 5) M. Kira, *et al.*, *Cryst. Growth Des.*, **2024**, 24, 3133-3139.

Synthesis of Titanium Nitride Semiconductor Nanocrystals

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Keywords: Titanium nitride; Nanocrystals; band gap; Photoluminescence; non-toxic

Semiconductor nanocrystals (NCs) of metal chalcogenides, and lead halide perovskites show excellent optical and electronic properties and are promising for solar cells, light emitting diodes, and photodetectors. However, these NCs carry toxic ions such as Cd, Hg, and Pb. Therefore, it is necessary to develop bandgap-tunable and luminescent NCs with nontoxic chemical compositions for sustainable applications. Titanium nitride (TN) NC is a promising candidate. However, TNNC synthesis requires sophisticated methods¹ or high temperatures (>1000 °C).² In this study, we demonstrate a facile low-temperature synthesis of TNNCs showing red photoluminescence (PL).

Fig. 1a shows a scheme of the TNNC synthesis. Titanium tetrachloride (TiCl₄) and sodium amide (NaNH₂) are heated in toluene at 90 °C. The obtained titanium amide is heated in hexadecane at 280 °C for 30 min. Both reactions were carried out under the argon atmosphere. After cooling down the reactants to room temperature, oleyl amine was added and purified by centrifugation. The prepared TNNCs are characterized using electron microscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. We also report the excitation and PL spectra of the TNNC colloidal solution (Fig. 1b). These NCs show a broad absorption band and a gaussian emission band. We discuss the excitonic properties and optical bandgap of the TNNCs.

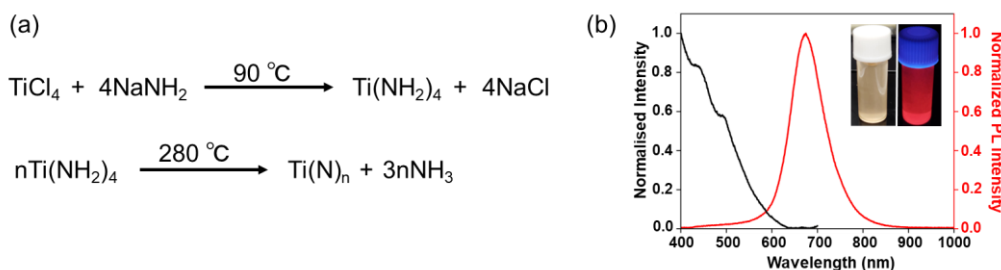


Fig 1. (a) A scheme of the TNNC synthesis. (b) Excitation ($\lambda_{\text{PL}} = 750$ nm) and PL spectra ($\lambda_{\text{ex}} = 400$ nm) of a TNNC solution. Inset: photographs of a TNNC solution under room light and UV light.

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- 2) R. A. Karaballi, G. Humagain, B. R. A. Fleischman, M. Dasog, *Angew. Chem. Int. Ed.*, **2019**, 58, 3147–3150.

Synthesis and Study of NHC Functionalized Diarylethene Ligand for Photoswitchable Catalysis

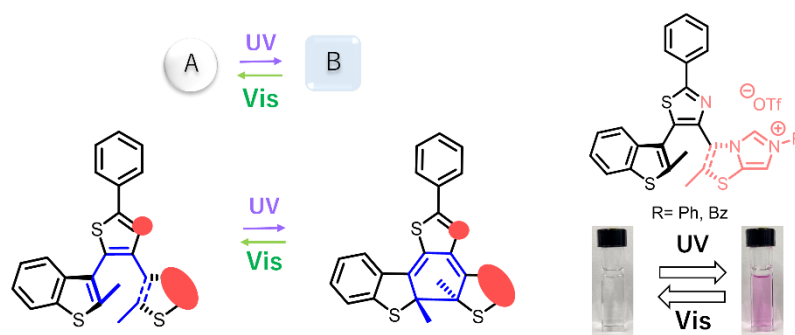
(¹Tokyo University of Agriculture and Technology, ²Nara Institute of Science and Technology, ³Ibaraki University, ⁴Rennes Institute of Chemical Science)
 ○Marine Louis^{1,2}, Taihei Kanou², Makoto Machiyama³, Lucie Jarrige⁴, Seiji Mori³, Tsuyoshi Kawai².

Keywords: photochromism, photophysics, organic chemistry, metal complex

This research aims to synthesize new, low-cost and environmentally friendly catalysts based on cheap earth-abundant metals (such as iron, nickel, and manganese) whose structures can be externally controlled through light irradiation. To do so, we focus on the development of photochromic ligands, more particularly on diarylethene. Indeed, upon UV light-irradiation, these compounds undergo chemical bond rearrangement known as photocyclization, resulting in electronic and structural changes, which dramatically alter their intrinsic properties. ^[1]

Although previous examples of terarylene-based ligands applied to photoswitch catalysis have been reported, most are limited to the ON/OFF control of the catalytic activity even though examples of enantiodivergence or reaction specificity have been highlighted ^[2].

In this presentation we will introduce a new NHC-carbene functionalized terarylene, whose coordination site is located close to the photoreactive carbons to maximize both electronic and steric variations to optimize the impact on the metal center and its coordination sphere. Synthesis, theoretical and photophysical analysis will be discussed along with preliminary complexations trials.



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