Academic Program [Oral B] | 11. Organic Chemistry -Structural Organic Chemistry-：Oral B

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[E1113-2vn] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Kazuo Tanaka, Yasunori Matsui

Japanese
3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC
[E1113-2vn-01]

Synthesis and Optical Evaluation of Gallium-Fused Azobenzene Complexes

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English
4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC
[E1113-2vn-02]

Solvent-directed, pressure-controllable chemosensor: A case of helical anthracene dimer

〇Tomokazu Kinoshita[1], Kota Watanabe[1], Eiji Tsurumaki[1], Shinji Toyota[1], Gaku Fukuhara[1] (1. Tokyo Tech)

English
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[E1113-2vn-03]

Development of Squaraine-Based Hole-Collecting Monolayer Materials for Perovskite Solar Cells

〇Shota Hira[1], Minh Anh Truong[1], Tomoya Nakamura[1], Richard Murdey[1], Atsushi Wakamiya[1] (1. Kyoto University, Institute for Chemical Research)

Japanese
4:55 PM - 5:15 PM JST | 7:55 AM - 8:15 AM UTC
[E1113-2vn-04]

Development of Organic Triboluminescence Materials Based on Polar Crystals

〇Takuya Ogaki[1], Yasunori Matsui[1], Hiroshi Ikeda[1] (1. Osaka Metro. Univ.)

縮環型アゾベンゼンガリウム錯体の合成と光学特性評価

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Synthesis and Optical Evaluation of Gallium-Fused Azobenzene Complexes

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Azobenzene is known as a non-emissive molecule due to its highly efficient photoisomerization, and therefore luminescent materials based on the azobenzene moiety have been hardly reported. Kawashima *et al.* found that the coordination of boron atom to the azobenzene scaffold suppressed the photoisomerization and permitted the electronic transitions, resulting in excellent fluorescence. We have developed typical element complexes with the ring-fused structure based on the tridentate azobenzene ligand. These complexes exhibited unique electronic states and fluorescent properties originating from heteroatom-specific structures. Boron-fused azobenzene complexes showed unique solid state luminescence derived from the four-coordinated tetrahedron structure. In addition, tin-fused complexes expressed the outstanding narrow energy gap originating from 3c–4e bond and Sn–N coordination, and exhibited vapochromic luminescence triggered by alteration of the coordination number from five to six at the tin atom. In this work, we focus on gallium, one of the high periodic elements of the group 13, and will explain the synthesis and optical property of the luminescent gallium-fused azobenzene complex.

Keywords : Gallium; Azobenzene; Fluorescence; π-Conjugated system

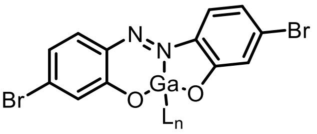

Figure 1. Chemical structure of a gallium-fused azobenzene complex.

アゾベンゼンはその高効率な光異性化のために非発光性であることが知られており、発光性の π 共役系骨格としての検討は進んでいない。一方川島らは、アゾベンゼンにホウ素を配位させることで、光異性化の抑制及び電子遷移の許容化に基づき、発光性分子となることを報告した[1]。当研究室では、アゾベンゼン三座配位子を用いた縮環構造を有する典型元素錯体を設計し、ヘテロ元素特有の構造に由来する機能性発光材料の創出に取り組んできた。13 族元素のホウ素を導入すると、四配位四面体構造に基づく特異な固体発光性を示すことを見出した[2]。また、14 族高周期元素の Sn を導入し、五配位三方両錐型の超原子価結合による狭エネルギーギャップ性や、スズ原子の配位数変化に伴うベイポクロミズム特性を明らかにした[3]。13 族高周期元素は未開拓であるが、ホウ素錯体と類似した固体発光性、及びスズと類似した高周期元素特有の光学物性の発現が期待される。そこで本研究では、13 族高周期元素の一つであるガリウムに注目し、縮環型アゾベンゼンガリウム錯体を創出した。発表では化合物の合成及び光学特性について詳述する。

1) J. Yoshino, N. Kano and T. Kawashima, *Chem. Commun.* **2007**, 559–561.
2) M. Gon, K. Tanaka, Y. Chujo, *Angew. Chem. Int. Ed.* **2018**, *57*, 6546–6551.
3) M. Gon, K. Tanaka, Y. Chujo, *Chem. – Eur. J.* **2021**, *27*, 7561–7571.

Solvent-directed, pressure-controllable chemosensor: A case of helical anthracene dimer

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Keywords: Pressure-Responsive Chemosensor; Hydrostatic Pressure Spectroscopy; Anthracene

The exploration of a pressure-responsive chemosensor is of particular significance in current multidisciplinary chemistry from the viewpoints of mechanoscience. So far, we have developed such chemosensors that are susceptible to hydrostatic pressure in solutions.[1] Of these, an anthracene-fused helicene, **[4]HA** (Fig. 1a), shows ratiometric pressure-responsive fluorescence changes upon the hydrostatic pressurization. The ratiometry in **[4]HA** is caused by the [4+4] photocyclodimerization of the intramolecularly π-π stacked anthracenes.[2] In this study, we focused on a pseudo-helicene dimer, **[2]HA$_2$** (Fig 1b) that is linked with two fused anthracene skeletons (**[2]HA**) via a single bond, which is believed to exhibit a solvation-dependent pressure sensitivity. Interestingly, as shown in Fig. 1c, **[2]HA$_2$** showed a distinctive pressure-induced fluorescence response. The fluorescence responses in some solvents are strongly dependent on solvent polarity estimated by E_T value; the response sign (ΔI) inverted at the border of E_T as 40 kcal mol^{-1}, shown in Fig. 1d. The excited-state dynamics (k_f and k_{nr}) of **[2]HA$_2$** under hydrostatic pressures supports the origins controlling pressure-induced solvation-driven transition states. It should be therefore noted that such interesting chemosensory responses are originated from the excited-state dynamics greatly involving pressure-induced microenvironmental polarities.

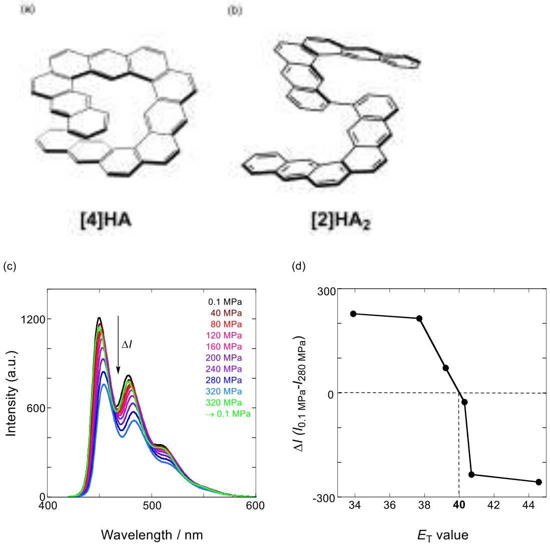


Figure 1. Chemical structures of helical anthracenes ((a) **[4]HA** and (b) **[2]HA$_2$**). (c) Fluorescence spectra of **[2]HA$_2$** in dichloromethane (λ_{ex} 412 nm, 57 μM) at room temperature, measured in a high-pressure cell. (d) Hydrostatic pressure-induced ΔI ($I_{0.1MPa}$ - I_{280MPa}).

1) Mizuno, H.; Fukuhara, G. *Acc. Chem. Res.* **2022**, *55*, 1748–1762. 2) Kinoshita, T.; Fujise, K.; Tsurumaki, E.; Toyota, S.; Fukuhara, G. *Chem. Commun.* **2022**, *58*, 3290–3293.

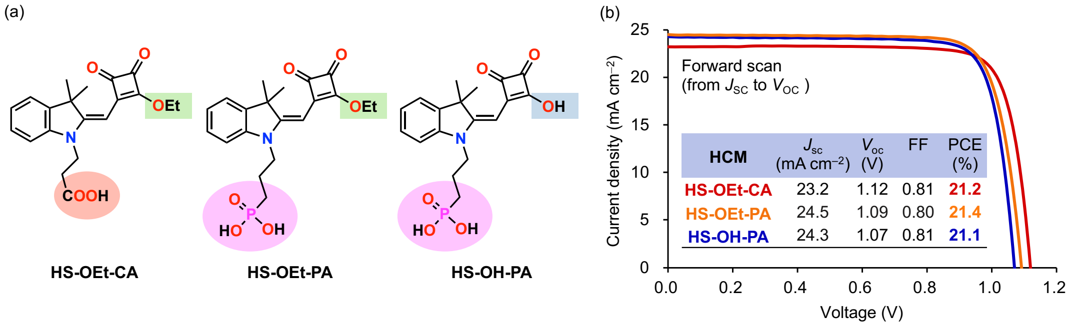
Development of Squaraine-Based Hole-Collecting Monolayer Materials for Perovskite Solar Cells

([1]*Institute for Chemical Research, Kyoto University*) ○Shota Hira,[1] Minh Anh Truong,[1] Tomoya Nakamura,[1] Richard Murdey,[1] Atsushi Wakamiya[1]

Keywords: Perovskite Solar Cell; Hole-Collecting Material; Monolayer; Squaraine; Chemisorption

Recently, chemically adsorbed hole-collecting monolayers (HCMs) with their ease of processing and high performance, have attracted great attention in order to further improve the performance of perovskite solar cells (PSCs).[1,2]

In this study, we designed and synthesized a series of half-squaraine derivatives (**HS-OEt-CA**, **HS-OEt-PA**, and **HS-OH-PA**, Figure 1a) as HCM materials. The cyclic voltammetry measurements in DMF solution revealed that compared to ethoxy-substituted **HS-OEt-CA** and **HS-OEt-PA**, hydroxyl-contained **HS-OH-PA** shows a lower oxidation potential, indicating the existence of an anionic form generated from the deprotonation of the squaric acid moiety. These molecules were found to adsorb on the surface of transparent conductive metal oxide electrodes to form a monolayer. According to photoelectron yield spectroscopy, the ionization potentials of **HS-OEt-CA**, **HS-OEt-PA**, and **HS-OH-PA** adsorbed ITO were estimated to be 5.54, 5.50, and 5.33 eV, respectively, which are shallower than the valence band (VB) of the perovskite material ($Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$, VB = 5.56 eV). PSCs using these half-squaraine derivatives as HCMs were fabricated and evaluated. All devices showed high power conversion efficiencies of over 21% (Figure 1b). **HS-OEt-CA**-based devices exhibit suppressed interfacial non-radiative recombination and higher open-circuit voltage (V_{OC}) than devices using phosphonic acid-substituted HCMs. In this presentation, molecular design, characterization, and device evaluation will be discussed in detail.



HCM	J_{sc} (mA cm⁻²)	V_{oc} (V)	FF	PCE (%)
HS-OEt-CA	23.2	1.12	0.81	**21.2**
HS-OEt-PA	24.5	1.09	0.80	**21.4**
HS-OH-PA	24.3	1.07	0.81	**21.1**

Figure 1. (a) Chemical structures of the half-squaraine derivatives. (b) *J*–*V* curves of the perovskite solar cells using the half-squaraine derivatives.

1) A. Al-Ashouri, S. Albrecht et al., *Science* **2020**, *370*, 1300.
2) M. A. Truong, A. Wakamiya et al., *J. Am. Chem. Soc.* **2023**, *145*, 7528.

極性結晶を基盤とする有機トリボルミネッセンス材料の開発

（阪公大院工）○大垣 拓也・松井 康哲・池田 浩

Development of Organic Triboluminescence Materials Based on Polar Crystals

(*Grad. Sch. of Eng., Osaka Metro. Univ.*) ○Takuya Ogaki, Yasunori Matsui, Hiroshi Ikeda

Triboluminescence (TL) is a luminescent phenomenon induced by mechanical stimuli. TL materials require both highly-luminescent properties in the solid state and organic polar crystals with a spontaneous polarization. However, it is difficult to rationally design such organic materials. To overcome the difficulty, we have developed organic TL polar crystals based on a host–dopant system.[1] As an alternative strategy to develop organic TL materials, in this work, we focused on the crystal symmetry and comprehensively explored organic TL materials among solid-state luminescent materials. Among various asymmetric diaryl keto-enols **1-R** (Fig. 1b), crystals of **1-*n*-Pr** with *n*-Pr group exhibit yellow TL upon mechanical stimuli (Fig. 1c) and belong to polar crystal with a space group of $P2_1$ (Fig. 1d). Moreover, TL-active polar crystals were newly found among other solid-state luminescent materials such as organoboron complexes. From these findings, it is found out that it is important to focus on both the solid-state luminescence and the crystal symmetry for developing new organic TL materials.

Keywords: Triboluminescence; Mechanoluminescence; Polar Crystals; Solid-state Luminescence; Organoboron Complexes

トリボルミネッセンス（TL，Fig. 1a）は，機械的刺激による発光現象である．有機 TL 材料には固体状態での高い発光性に加えて，自発分極をもつ有機極性結晶（Fig. 1a）が必要とされるが，そのような材料の合理的設計は一般に困難である．この問題に対して，我々は最近ホスト–ドーパント系有機 TL 材料を開発した[1]．本研究ではこれに代わる有機 TL 材料開発戦略として結晶の対称性に着目し，固体発光材料の中から TL 材料の網羅的探索を行った．その結果，非対称ジアリールケトエノール **1-R**（Fig. 1b）のうち，*n*-Pr 基を有する **1-*n*-Pr** の結晶は機械的刺激により黄色 TL を示し（Fig. 1c），$P2_1$ の空間群をもつ極性結晶に属することがわかった（Fig. 1d）．また，この他に有機ホウ素錯体などの他の固体発光材料の中からも，新たな有機 TL 材料が見つかった．これらの知見から，新たな有機 TL 材料開発には，固体発光特性と結晶の対称性の両方に着目することが重要であることがわかった．

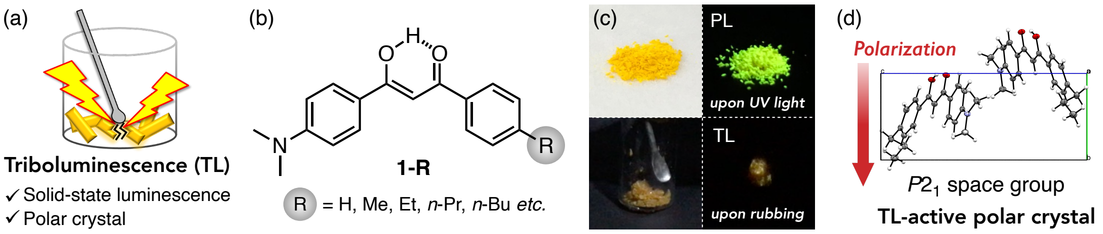


Fig. 1. (a) An illustration and fundamental requirements of organic TL materials, (b) molecular structure of **1-R**, (c) photographs of photoluminescence (PL) and TL of **1-*n*-Pr**, and (d) the packing structure of **1-*n*-Pr**.

1) 大垣，松井，池田，*日本化学会第 103 春季年会(2023)予稿集*，K603-1pm-05，**2023**.