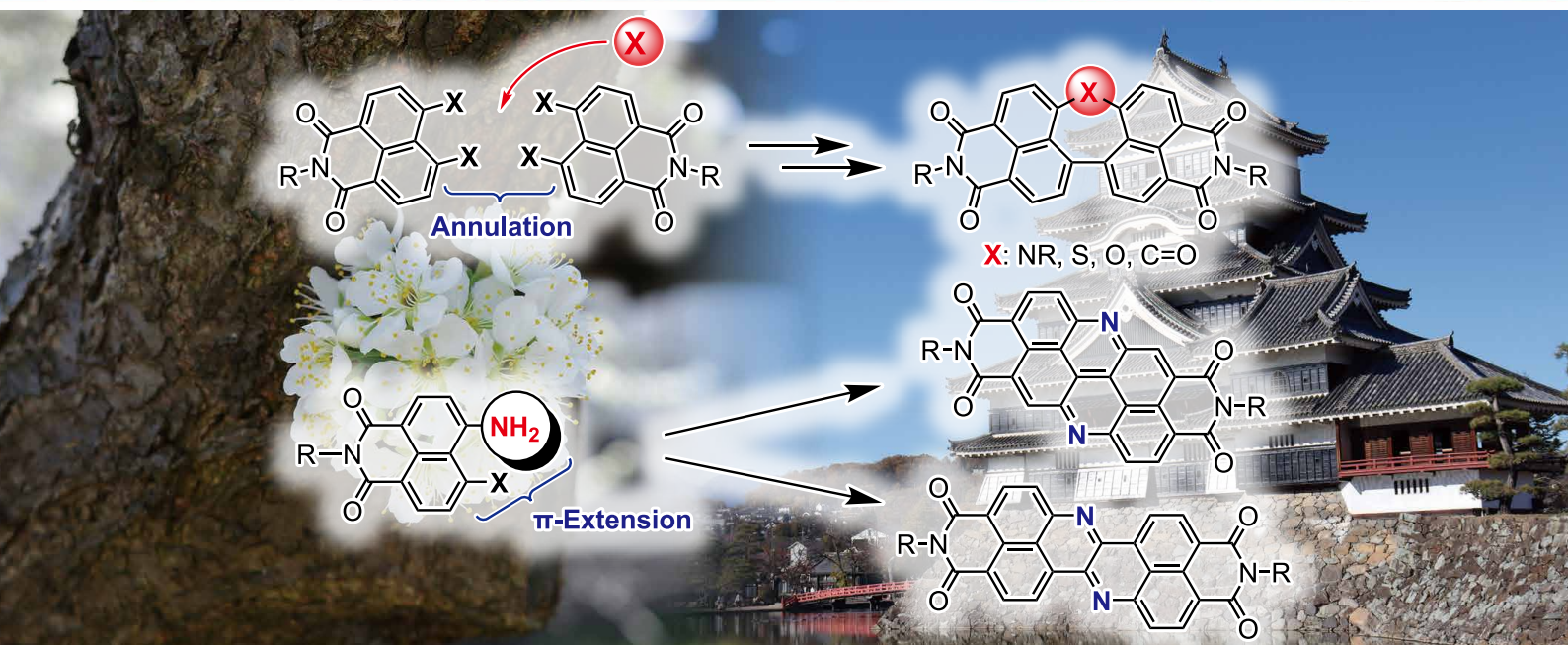


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Research Article

Development of typical-element-doped functional π -systems consisting of naphthalene monoimide units

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1. Introduction

π -Conjugated molecules are key components of advanced materials such as organic-based electronics. The function of these compounds is closely related to their delocalized π -electrons, which can be precisely modulated by introducing functional groups on the periphery of the compound. The characteristics of such designed molecules strongly rely on the inherent electronic nature of the parent skeleton, highlighting the importance of selecting an appropriate motif molecule. Such π -conjugated molecules should satisfy two criteria: (1) they intrinsically exhibit desirable electronic properties and (2) their structures are readily transformable via well-established organic

transformations.

π -Conjugated molecules are intrinsically electron-donors because the π -electrons are loosely bound to the core. Electron-accepting π -systems are thus relatively rare, underlining the need to develop novel electron-accepting π -systems. Furthermore, electron-accepting π -systems are attractive because high electron affinity leads to excellent atmospheric stability, electron-transporting properties, and short molecular contacts, all useful features for the construction of next-generation materials such as organic-based electronics and supramolecular assemblies.

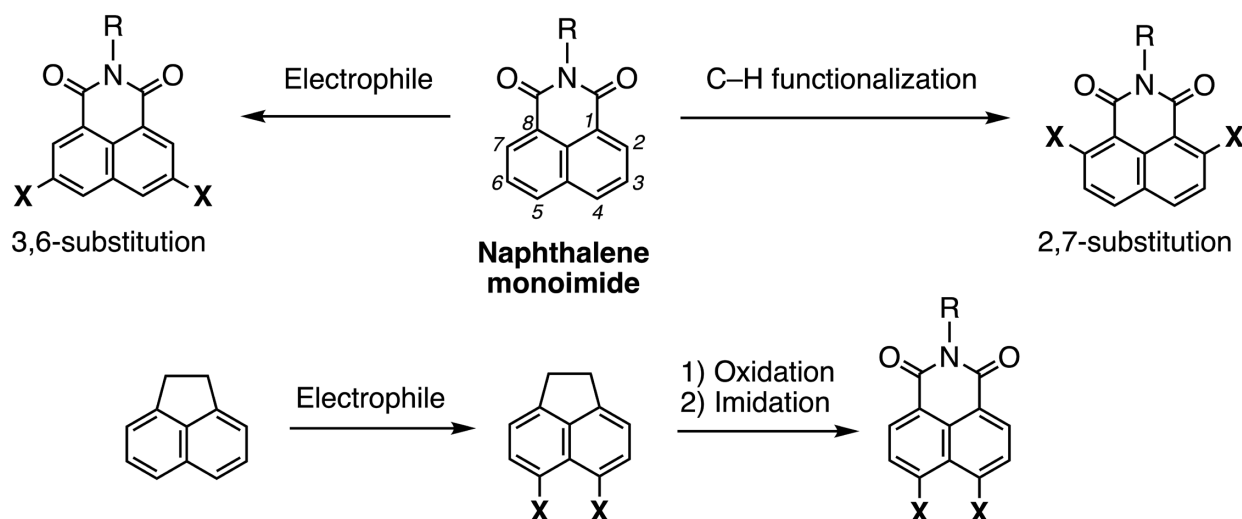


Figure 1. Syntheses of peripherally functionalized NMIs.

Our research has focused on naphthalene monoimide (NMI) as a motif to create novel electron-accepting π -systems, due to its several advantageous features. First, various synthetic strategies to peripherally functionalized NMIs have been developed (**Figure 1**). The electrophilic aromatic substitution of NMI selectively affords the 3,6-functionalized derivative, with the transition-metal-catalyzed direct C–H functionalization reaction proceeding at the *ortho*-positions of the carbonyl group (2,7-positions).¹ The 4,5-functionalized NMIs are accessible via two-step transformations from acenaphthene: electrophilic substitution followed by imidation. The second feature of NMI is the high electron affinity derived from the imide group, with π -extended analogues such as perylene bisimide (PBI) exhibiting excellent electron transporting properties in the solid state.² Donor-functionalized NMI derivatives exhibit solvatochromism in response to solvent polarity, which is useful for designing environment-responsive bioimaging luminophores.³ The third attractive feature of NMI is that

its solid-state arrangement can be controlled precisely by changing the imide-substituents. This strategy has been frequently utilized in the development of high-performance organic semiconductors and functional supramolecular assemblies.⁴

Given the above, we selected NMI as the starting compound and applied our original molecular design guidelines for creating novel functional π -conjugated molecules. Herein, we introduce two strategies for generating useful high electron affinity compounds (**Figure 2**). In the first strategy, two NMI units are linked by a reactive moiety at the 4-positions, and then the linked complex is subjected to annulation at the 5-position to provide element-inserted PBIs as new nonplanar PBI derivatives. In the second strategy, we extended the π -system of NMI by introducing electronegative imine-type nitrogen atoms, allowing the dual incorporation of imide groups and imine-type nitrogen atoms to provide extremely high electron affinity.

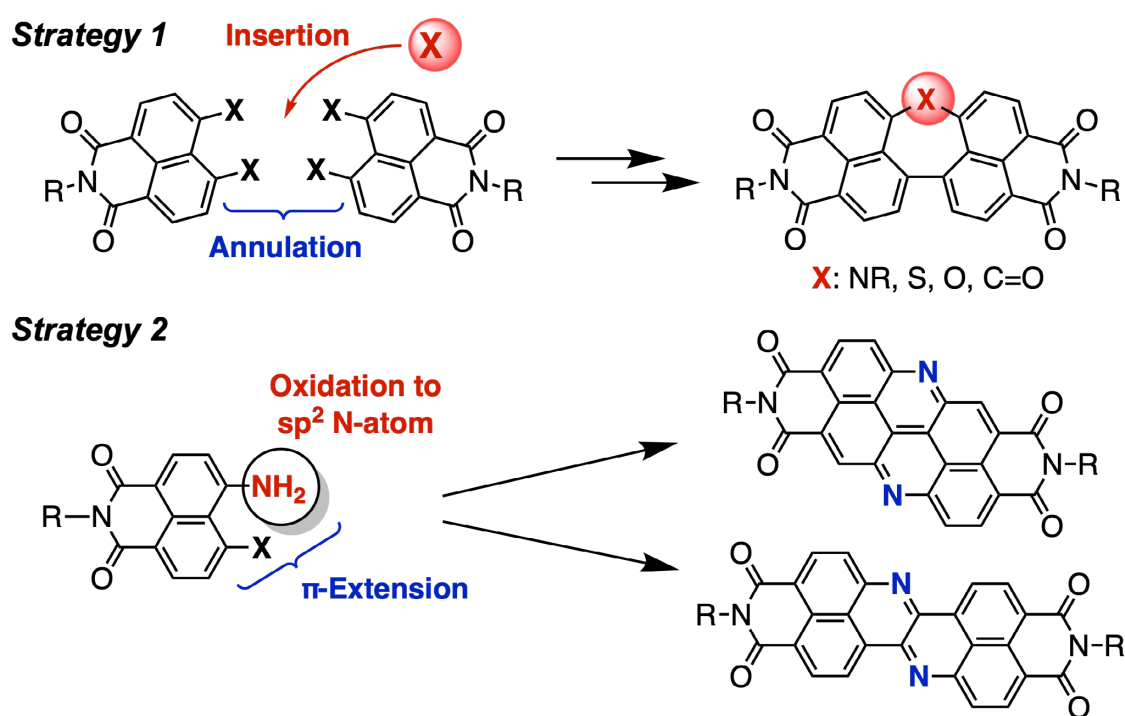


Figure 2. Molecular designs using NMI as a building block.

2. Element-inserted PBIs

PBI adopts a rigid, planar structure with attractive photophysical properties and high electron affinity, but the planar structure and high electron-deficiency enhance intermolecular interactions, resulting in low solubility in common organic solvents. In contrast, twisted PBI derivatives have a nonplanar structure due to steric repulsion at the bay area, and exhibit high solubility.^{5–8} Such nonplanar PBIs function as solution-processable

n-type organic semiconductors and non-fullerene electron-transporting materials for use in organic solar cells. We therefore proposed a new strategy for designing nonplanar PBI derivatives by inserting various elements at the linkage site. This section describes the synthesis and properties of nitrogen-, sulfur-, oxygen-, and carbon-inserted PBIs.

2-1. Insertion of nitrogen

The introduction of an electron-rich amine-type nitrogen atom on highly electron-accepting PBI cores confers intramolecular charge transfer (ICT) properties, providing molecules that undergo large conformational changes in the photoexcited state and a large dipole moment, two features important for stimuli-responsive molecules.⁹ The NH group also acts as a hydrogen-bonding donor. The substituent on the nitrogen atom controls the solid-state arrangement, essential for the design of effective electron transport materials for organic solar cells.^{10,11} Then, we have designed a nitrogen-inserted PBI derivative.¹²

Figure 3a shows the synthesis of nitrogen-inserted PBIs. An intermolecular C–I/C–Br homo coupling reaction of 4-bromo-5-iodo-NMI **1** using copper(I) 2-thiophenecarboxylate provided the corresponding dimers **2**. Buchwald–Hartwig amination of **2** with octylamine, aniline, and 4-methoxybenzylamine afforded the corresponding nitrogen-inserted compounds **3a**, **3b**, and **3c**, respectively. Treatment of **3c** with an excess of anisole and trifluoroacetic acid deprotected the 4-methoxybenzyl group to provide NH-inserted compound **3d**.

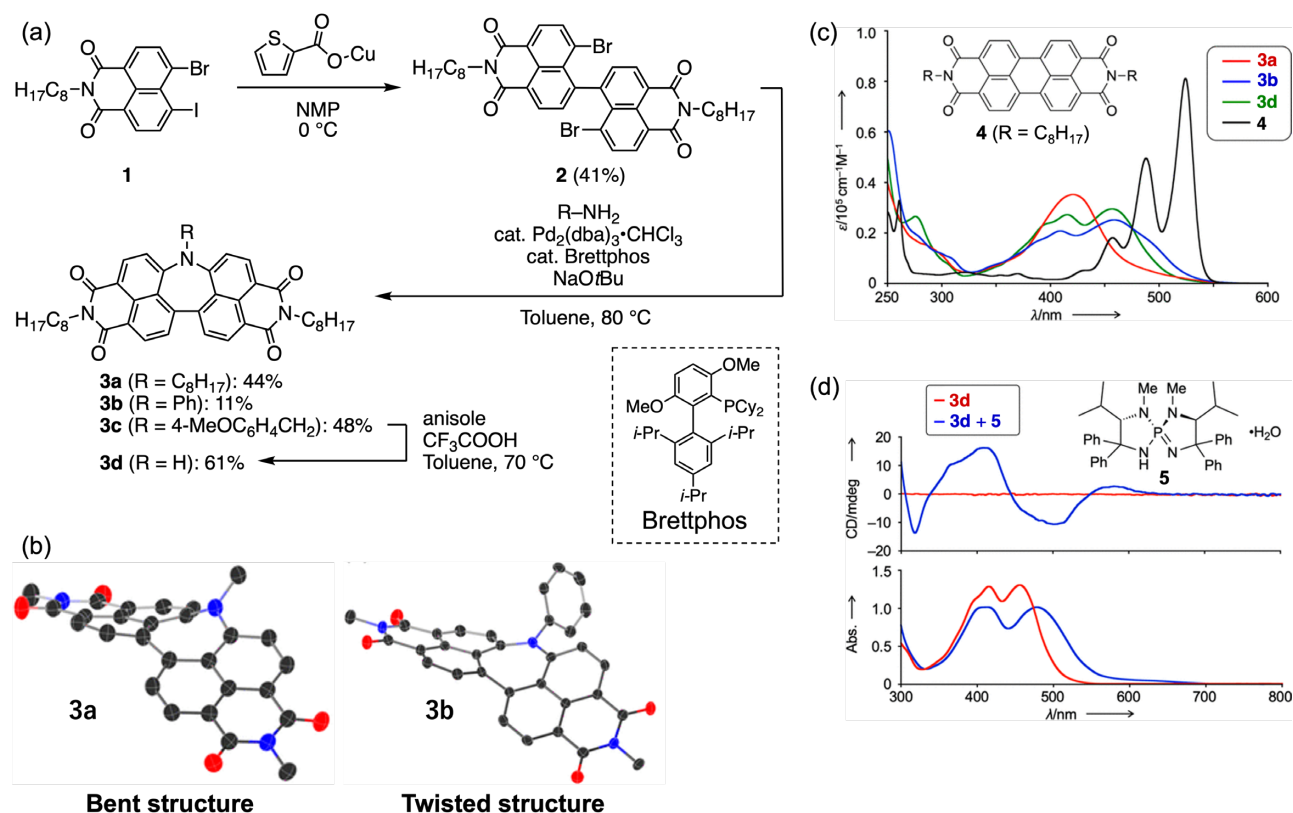


Figure 3. (a) Synthesis of nitrogen-inserted PBIs.
 (b) X-ray crystal structure of **3a** and **3b**. Alkyl groups on the nitrogen atom are partially omitted.
 (c) UV/vis absorption spectra of PBI and nitrogen-inserted PBIs.
 (d) Chirality induction of NH-inserted **3d** with optically active hydrogen-bonding acceptor **5**.

X-ray structural analysis revealed that octylamine-inserted **3a** and aniline-inserted **3b** adopt different nonplanar structures (Figure 3b). Compound **3a** has a folded structure in which the two NMI units are not equivalent, whereas compound **3b** adopts a symmetrically twisted structure. The structural difference between these two molecules was evident in their absorption spectra: octylamine-inserted **3a** exhibited a red-shifted absorption spectrum compared to aniline-inserted **3b** (Figure 3c).

Interestingly, the structure of the nitrogen-inserted PBI can be controlled by external stimuli, such as by

applying an electric field or adding hydrogen-bonding acceptors. Octylamine-inserted **3a** has a dipole moment because the two NMI moieties are not equivalent due to its folded structure. The application of an external electric field modulated the structural dynamics of **3a**. NH-inserted derivative **3d** functioned as a hydrogen-bonding donor toward chiral iminophosphorane **5**,¹³ a compound developed by Prof. Ooi and Prof. Uraguchi. Treatment of **3d** with **5** provided a complex in toluene whose CD spectrum exhibited a Cotton effect (Figure 3d), indicating that complex formation with a chiral hydrogen-bonding acceptor controls the direction of

helicity in NH-inserted PBI **3d**.

During the above study, we also synthesized a nitrogen-bridged NMI dimer **8**, which exhibits aggregation-induced emission (AIE) (Figure 4).¹⁴ The key to generating AIE is the suppression of non-radiative deactivation via a twisted ICT (TICT)

structure in the solid. Selective functionalization at the *ortho*-position of the carbonyl groups of **8** enabled tuning of the emission color to provide red-emission. Recently, Prof. Xia and co-workers revealed that photoexcitation of **8** induces symmetry-breaking charge transfer.¹⁵

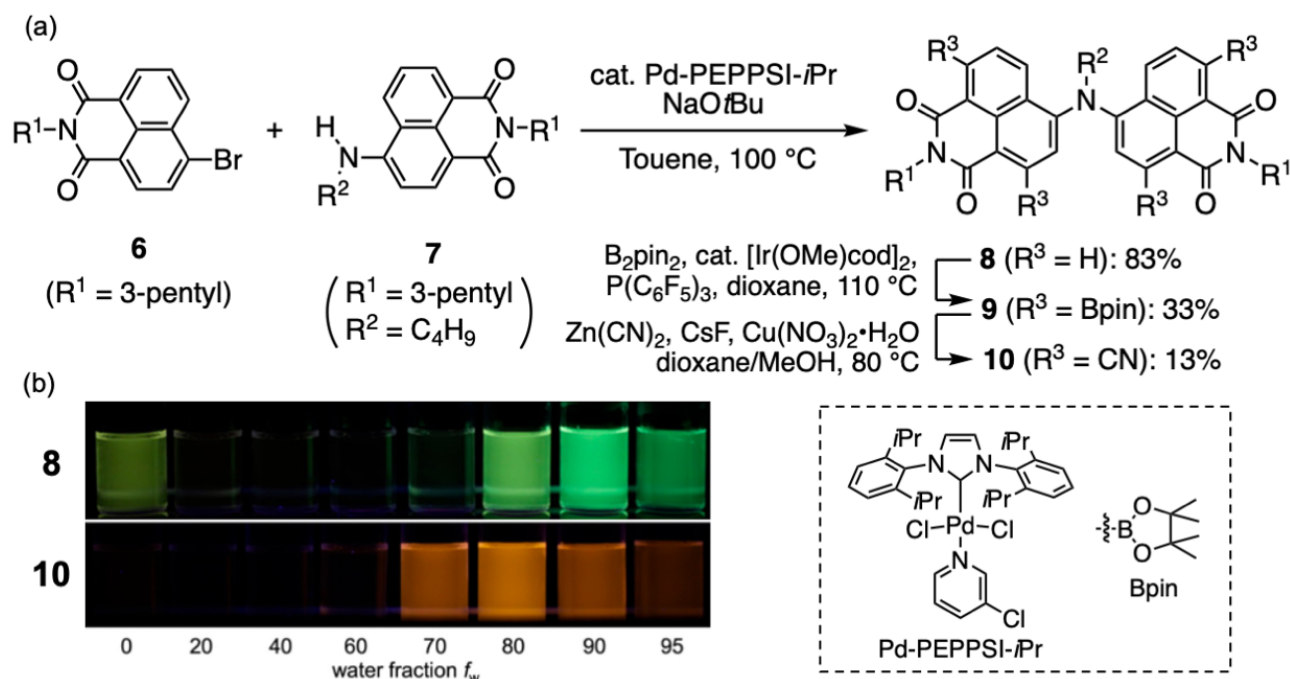


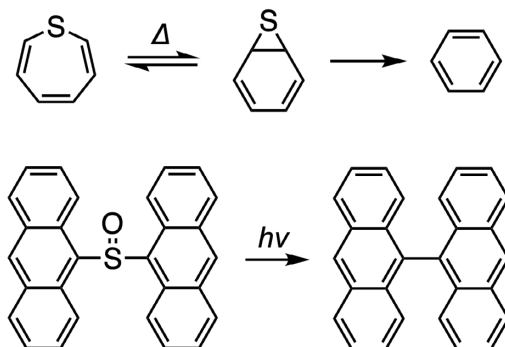
Figure 4. (a) Synthesis of nitrogen-bridged NM. (b) Photographs of THF/water solutions under photoirradiation.

2-2. Insertion of sulfur

Several organosulfur compounds undergo sulfur-extrusion reactions upon photoirradiation and/or heating. For example, thiophene undergoes a thermally induced pericyclic reaction to provide benzene following intermolecular collision.^{16,17} Photoirradiation of a 9-to-9' sulfoxide-bridged anthracene dimer gives

9,9'-bianthracene (Figure 5).¹⁸ We found that sulfur-inserted PBIs undergo sulfur extrusion reactions to give PBIs.¹⁹ This unique reaction strategy enables fabrication of thin films of PBI by solution processing.

Previous work



This work

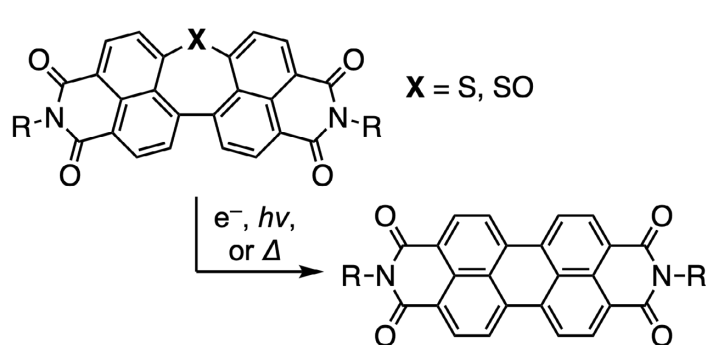


Figure 5. Sulfur extrusion reactions.

The synthetic strategies for sulfur-inserted PBI and the corresponding sulfoxide and sulfone are shown in Figure 6a. The nucleophilic aromatic substitution of 5,5'-bridged-4,4'-dibromo-NMI dimer **2** with sodium sulfide afforded sulfur-inserted PBI **11**. The sulfur unit of **11** was oxidized with *m*-chloroperoxybenzoic acid (*m*CPBA) to afford the corresponding sulfoxide **12**,

whereas the tungsten-catalyzed oxidation²⁰ of **11** with hydrogen peroxide provided sulfone **13**.

We have also developed a gram-scale synthetic strategy to access sulfur-inserted PBIs for the efficient synthesis of analogues with different substituents at the imide positions for imidization in the final step.²¹

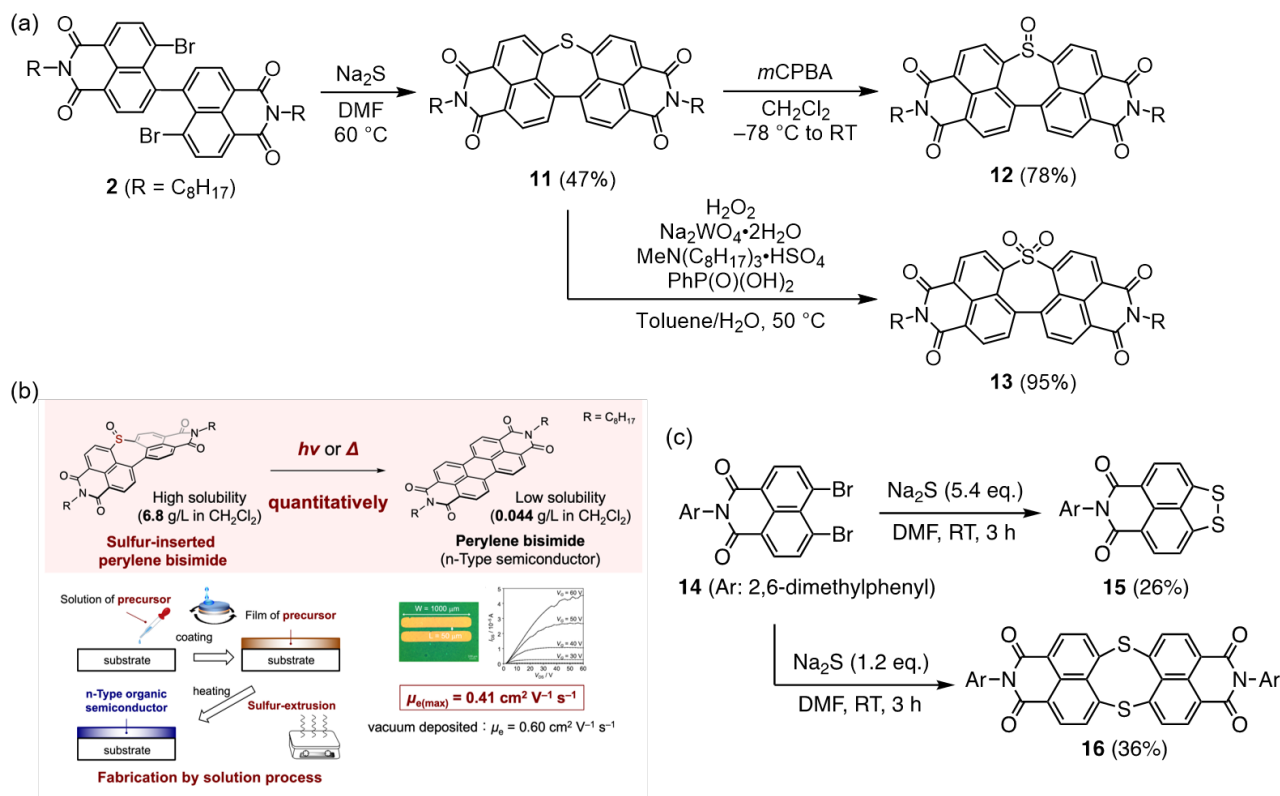


Figure 6. (a) Synthesis of sulfur-inserted PBIs.

(b) Fabrication of a thin film of PBI using sulfur-inserted PBI as a soluble precursor.

(c) Synthesis of doubly sulfur-inserted PBI.

Single-crystal X-ray analysis revealed that sulfur-inserted PBI adopts a nonplanar structure and accordingly sulfur-inserted PBI showed high solubility in common organic solvents. For example, the solubilities of sulfide-, sulfoxide-, and sulfone-inserted PBIs in dichloromethane are 2.9 g/L, 0.51 g/L, and 5.4 g/L, respectively, which are 150–1700 times higher than that of PBI (0.0033 g/L). Furthermore, subjecting sulfur-inserted PBI to photoirradiation, heating, and electron injection resulted in sulfur-extrusion reactions to afford PBI almost quantitatively. Finally, we examined the use of sulfur-inserted PBIs as a soluble precursor for PBI in collaboration with Prof. Yamada and Dr. Matsuo (Figure 6b). Sulfoxide-inserted PBI was

spin-coated onto a silicon substrate, and the obtained thin film was heated to induce the sulfur-extrusion reaction. The devices acted as n-type semiconductors with a maximum electron mobility value of $\mu_e = 0.41 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to that obtained by vacuum deposition ($\mu_e = 0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

We also synthesized a doubly sulfur-inserted PBI derivative that adopts a V-shaped structure (Figure 6c).²² The activation energy for inversion of the V-shaped structure is 30 kcal mol⁻¹. Disulfide-bridged NMI **15** was obtained as a by-product. Prof Xia and co-workers revealed that compound **15** undergoes ultrafast internal conversion by stretching the S–S bond.²³

2-3. Insertion of oxygen

The synthetic procedure for oxygen-inserted PBI is shown in Figure 7. The reaction of 5,5'-bridged-4,4'-dichloronaphthalene dicarboxylic anhydride dimer **17** with 2,4,6-trimethylaniline afforded imide-substituted compound **18**. Subsequently, oxygen-inserted PBI was synthesized by reaction with α -benzaloxime²⁴ under basic conditions.²⁵ Interestingly, oxygen-inserted PBI **19** underwent an oxygen-extrusion reaction upon electron injection with decamethylcobaltocene,

affording the radical anion of PBI. The crude mixture was treated with *p*-chloranil, giving PBI **20** in 63% yield. The dissociation energy of a C–O bond is quite high, and the Lewis basicity of the oxygen atom in diaryl ethers is low. Consequently, cleavage of a C–O bond is challenging.^{26,27} Our results provide fundamental insights into the development of a rational method for C–O bond transformation.

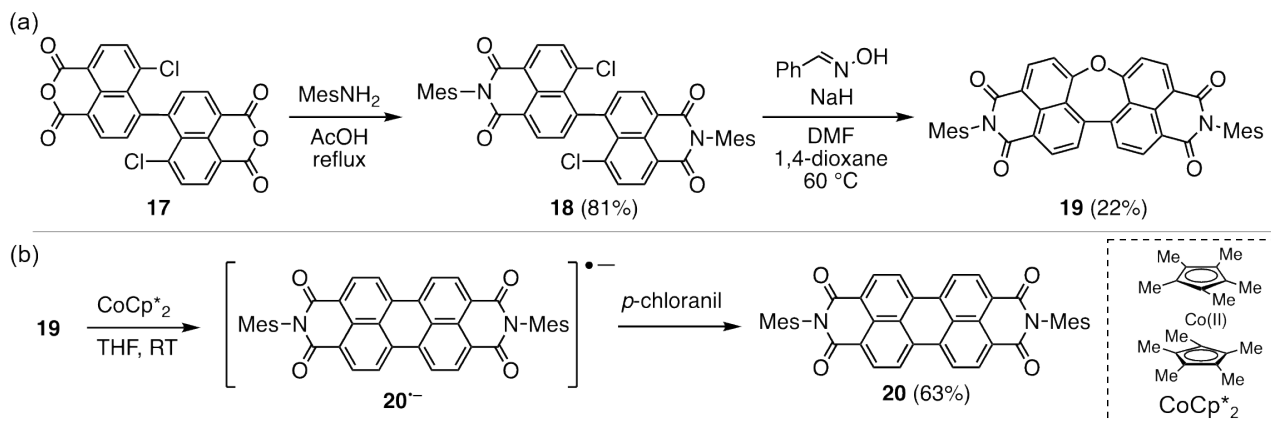


Figure 7. (a) Synthesis of oxygen-inserted PBI. (b) Oxygen-extrusion reaction via electron injection into oxygen-inserted PBI.

2-4. Insertion of carbon

Figure 8 shows the synthesis of carbon-inserted PBI. Treating 5,6-dibromoacenaphthene **21** with 1.0 equivalent of *n*-butyllithium afforded the corresponding mono-lithiated intermediate, which was coupled with 5-bromo-6-formylacenaphthene **22** to furnish bis(6-bromoacenaphthen-5-yl)methanol **23**. After oxidation of all the benzylic carbons in **23** with sodium dichromate, the reaction mixture was directly treated

with 2,4,6-trimethylaniline to furnish the corresponding carbonyl-bridged NMI dimer. Intramolecular Yamamoto coupling of **24** with bis(1,5-cyclooctadiene)nickel(0) provided carbonyl-inserted PBI **25**.²⁸ The carbonyl group was converted to a methylene group via Luche reduction, followed by treatment of triethylsilane and trifluoromethanesulfonic acid to provide methylene-inserted PBI **27**.

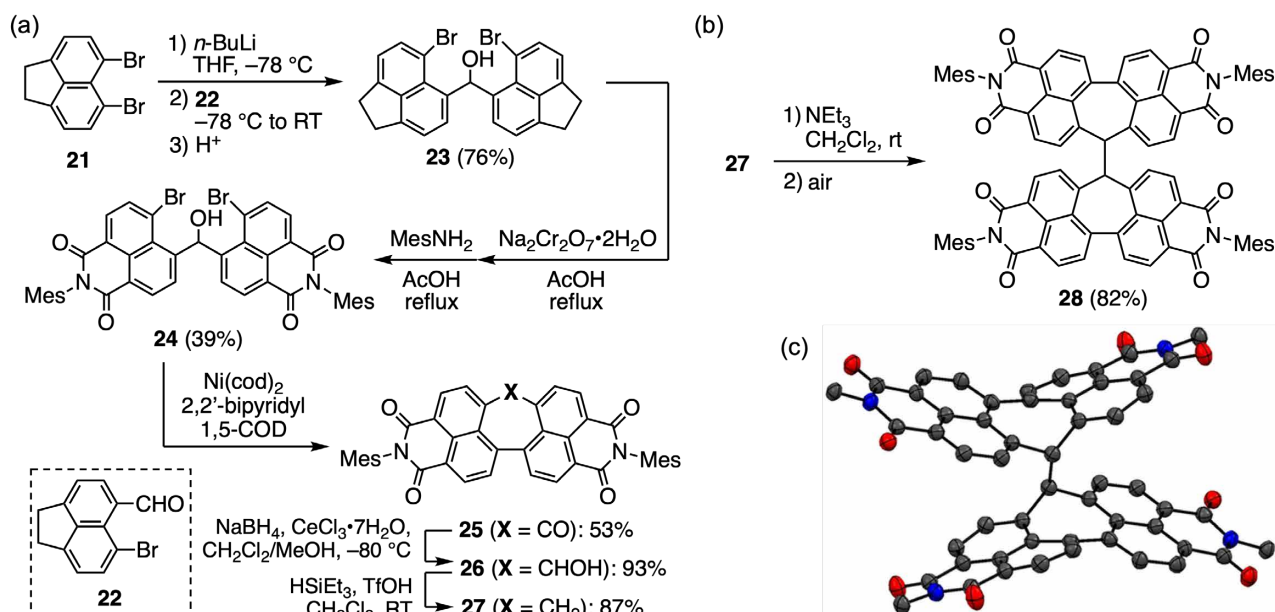


Figure 8. (a) Synthesis of carbon-inserted PBIs. (b) Reactivity of methylene-inserted PBI. (c) X-ray crystal structure of dimer **28**.

X-ray structural analysis revealed that both carbonyl- and methylene-inserted PBIs adopt nonplanar structures. Methylene-inserted PBI showed fluorescence with a quantum yield of 31%, whereas carbonyl-inserted PBI exhibited weak fluorescence with a quantum yield of 0.8%. Transient absorption spectroscopy suggested that photoirradiation of

carbonyl-inserted **25** provided the excited triplet species. Interestingly, the deprotonation of methylene-inserted PBI **27** followed by aerobic oxidation furnished dimer **28**, whose central methylene carbons are connected. This dimer **28** exhibited reversible C–C bond formation under electrochemical redox conditions (a *dyrex* reaction).

3. Dual incorporation of imine-type nitrogen atoms and imide substituents

There are two general approaches for designing highly electron-accepting π -systems. One is the introduction of electron-withdrawing peripheral substituents such as an imide group, as seen in PBI, and the second is the introduction of electronegative sp^2 -nitrogen atoms into the π -cores, as observed for an imine-doped pentacene that works as an n-type semiconductor.²⁹ The two strategies have generally been applied independently, although

there are several reports of the incorporation of both an electron-withdrawing group and an imine-type nitrogen atom.^{30,31} The latter resulting molecules show remarkably high electron affinity and work as an effective and air-stable n-type organic semiconductor. These findings prompted us to incorporate both an electron withdrawing group and an imine-type nitrogen atom into anthanthrene and zethrene.

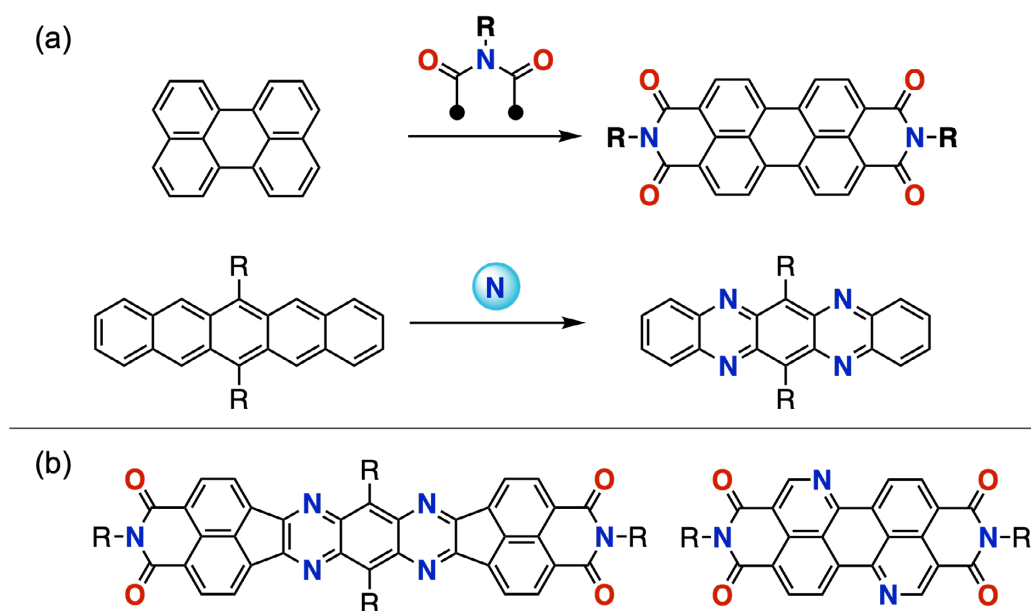


Figure 9. Guidelines for designing electron-accepting π -systems. (a) Incorporation of imide substituents and imine-type nitrogen atoms. (b) Previously reported molecules incorporating both an imide substituent and imine-type nitrogen atoms.

3-1. Acridino[2,1,9,8-*klmna*]acridine bisimide

Anthanthrene is a nanographene with a zig-zag edge structure³² and exhibits excellent photophysical properties and charge-transport behavior derived from its large π -system, leading to anthanthrene derivatives being studied as hole-transporting materials in organic solar cells.³³ Anthanthrene is thus potentially attractive as a building block for organic electronic materials. We previously designed acridino[2,1,9,8-*klmna*]acridine bisimide (AABI), which represents an anthanthrene derivative that incorporates both imide groups and imine-type nitrogen atoms.³⁴

The synthesis of AABI is shown in Figure 10. Nickel-catalyzed homo-coupling of 4-bromo-5-amino NMI **29** provided the corresponding dimer

30. Subsequent oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone and $\text{Sc}(\text{OTf})_3$ afforded AABI **31**. Electrochemical analysis showed that AABI exhibits a first reduction potential at -0.72 V (vs. Fc/Fc^+). In the solid state, *N*-alkyl derivatives adopt brickwork-type packing. Organic field-effect transistor (OFET) devices comprising AABI were fabricated by vacuum deposition. Phenethyl derivatives **31c** afforded a maximum electron mobility μ_{max} of $0.34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and single-crystal OFET devices showed a high electron mobility μ_e of $0.90 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Thus, the incorporation of imide groups and imine-type nitrogen atoms is conducive to the formation of robust n-type semiconductor molecules.

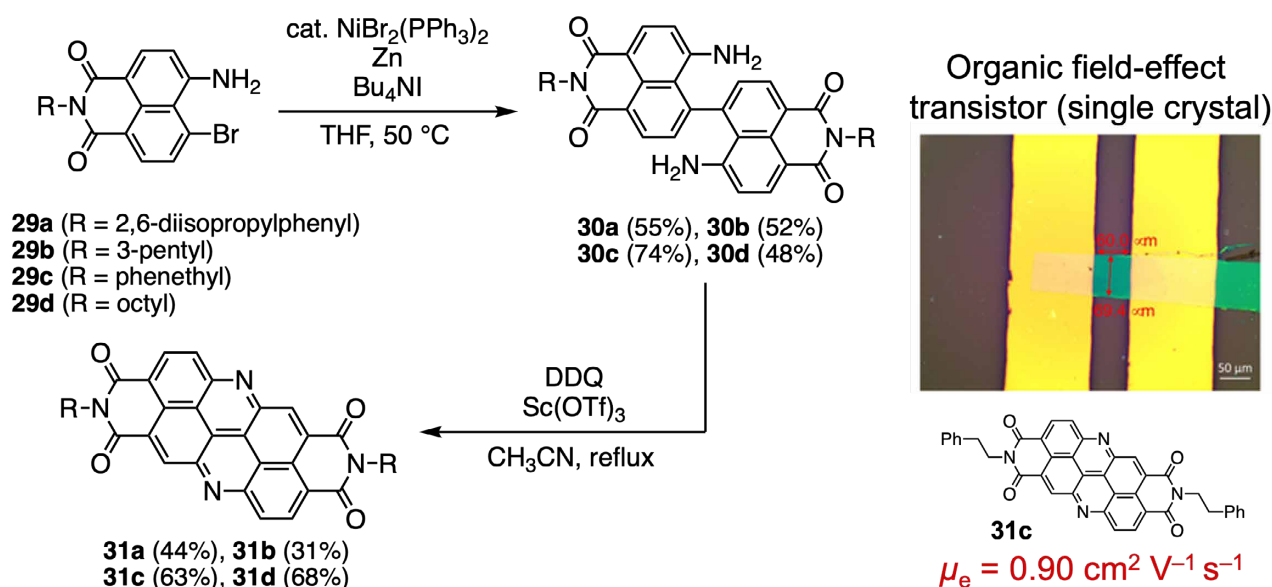


Figure 10. Synthesis and single-crystal OFET device comprising AABI.

3-2. Diazazethrene bisimide

Zethrene is a nanographene with a high reduction potential of -1.76 V ,³⁵ which is more positive than that of anthanthrene (-2.11 V).³² We formed an extremely electron-accepting π -system by functionalizing zethrene with imide groups and imine-type nitrogen atoms.³⁶

The synthetic procedure is shown in Figure 11. Migita–Kosugi–Stille cross-coupling of 4-amino-5-bromo NMI **29** with bis(trimethylstannyl)acetylene afforded alkyne-bridged dimer **32**. Pd-catalyzed intramolecular hydroamination of **32** gave enamine-form **33**. Treatment of **33** with bis(trifluoroacetoxy)-iodobenzene provided diazazethrene bisimide **34**. Interestingly, subjecting compound **33** to oxidation with DDQ provided not only compound **34** but also dimer **35**. Electrochemical measurements showed that diazazethrene bisimide and its dimer exhibit

first reduction potentials at -0.49 V and -0.36 V , respectively. Electron injection into diazazethrene bisimide **34** using cobaltocene afforded the dianion **36**, which is remarkably stable under ambient conditions. Treatment of diazazethrene bisimide **34** with bis(trimethylsilyl)dihydropyrazine afforded dihydro-form **37**. Interestingly, this hydrogenation could be induced using L-ascorbic acid, a weak reductant. Dihydro-form **37** and dianion **36** were reversibly transformed by the addition of acid and base. A vacuum-deposited field-effect transistor comprising **34b** was fabricated and exhibited a maximum electron mobility μ_e of $6.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in vacuum and $\mu_e = 5.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in air. The observed excellent mobility under air is likely due to the high electron affinity of diazazethrene bisimide.

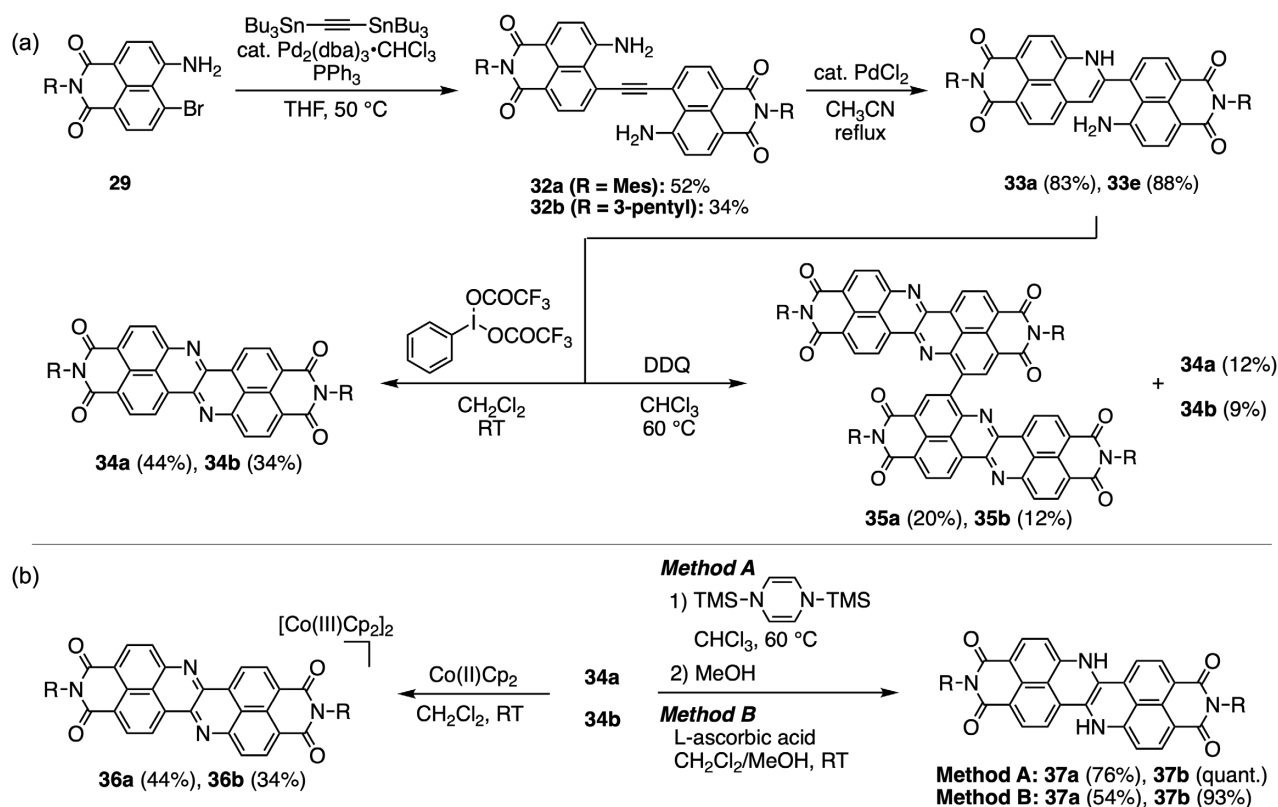


Figure 11. (a) Synthesis of diazazethrene bisimides and their dimers. (b) Reduction of diazazethrene bisimides.

Summary

This account summarized our developmental studies of novel functionalized π -systems using NMI as a building block. Section 2 presented element-inserted PBI derivatives with nitrogen, sulfur, carbon, and oxygen atoms. These compounds exhibit unique functions due to cooperation between the inserted elements and the compound's nonplanarity. Sulfur-inserted PBI functioned as a soluble precursor for PBI,

enabling the fabrication of an n-type semiconductor film using a solution process. In Section 3, we described the incorporation of imide- and imine-type nitrogen atoms into two nanographenes: anthanthrene and zethrene. The resulting compounds exhibit excellent electron affinity and thus function as effective n-type semiconductor materials.

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[Research fields] Structural organic chemistry, Organic synthesis.

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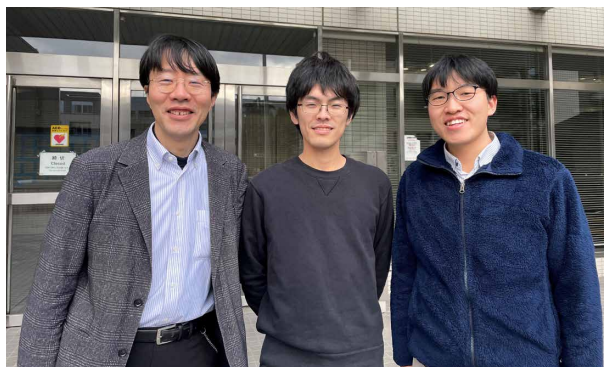
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(left: Prof. Shinokubo, center: Mr. Tajima, right: Dr. Fukui)

Related Products

| | | | | |
|--|-----|-------|-------|-------|
| Copper(I) 2-Thiophenecarboxylate (= CuTC) | | 1g | 5g | C2312 |
| Dicyclohexyl(2',4',6'-triisopropyl-3,6-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (= BrettPhos) | | | 250mg | D5664 |
| [1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene]-(3-chloropyridyl)palladium(II) Dichloride (= Pd-PEPPSI-iPr) | | 1g | 5g | B6199 |
| Bis(pinacolato)diboron (= B ₂ pin ₂) | 1g | 5g | 100g | B1964 |
| (1,5-Cyclooctadiene)(methoxy)iridium(I) Dimer (= [Ir(OMe)cod] ₂) | | 200mg | 1g | C2662 |
| Tris(pentafluorophenyl)phosphine (= P(C ₆ F ₅) ₃) | | 1g | 5g | T2484 |
| α-Benzaldoxime | 25g | 100g | 500g | B0011 |
| Bis(1,5-cyclooctadiene)nickel(0) | | | 5g | B6553 |
| 2,2'-Bipyridyl | 25g | 100g | 500g | B0468 |
| Triethylsilane | | 25mL | 250mL | T0662 |
| Scandium(III) Triflate | | 1g | 5g | T1663 |
| Palladium(II) Chloride | | 1g | 5g | P1489 |
| [Bis(trifluoroacetoxy)iodo]benzene | 5g | 25g | 100g | B1175 |

Chemistry Chat

Difficulties in Senior High School Chemistry Experiments

Toyo University Keihoku Senior High School

Hiroyuki Onuki

1. Introduction

Senior high school chemistry textbooks in Japan contain procedures and tips for student experiments. It is quite natural for teachers and students to expect that the experiments proceed as anticipated, since chemical experts supervise the textbooks. However, when we try the experiments, we sometimes encounter results that do not

meet our expectations and thus we do not reach a proper understanding of the subject. In addition, experiment time is limited because the time required for preparation and cleanup cannot be ignored. I would like to discuss these difficulties in senior high school chemistry.

2. Sublimation of Iodine

In senior high school "Basic Chemistry" course, students learn that sublimation is one of the methods for the separation of mixtures. Sublimation is a phenomenon in which a solid directly becomes a gas. For example, iodine and carbon dioxide, which are molecular crystals, easily sublime. However, if you put pieces of iodine in the bottom of a test tube or a beaker and heat it with a burner, you can observe not only purple vapor from solid iodine but also purple liquid of iodine. Heated iodine does not only become a gas directly from a solid, but also via a liquid. The melting point and boiling point of iodine are

114 °C and 184 °C, respectively. You can find solid iodine melts and sublimates. In this experiment, students observe not only sublimation but also melting. Students who have preconceptions that melting and sublimation occur separately are confused.

In the actual experiment, the sublimation technique is demonstrated to separate pure iodine from a mixture of sand and iodine.¹ It would be difficult to observe the liquid iodine in the sand. How ingenious the experiment is!



Figure 1. Sublimation of iodine

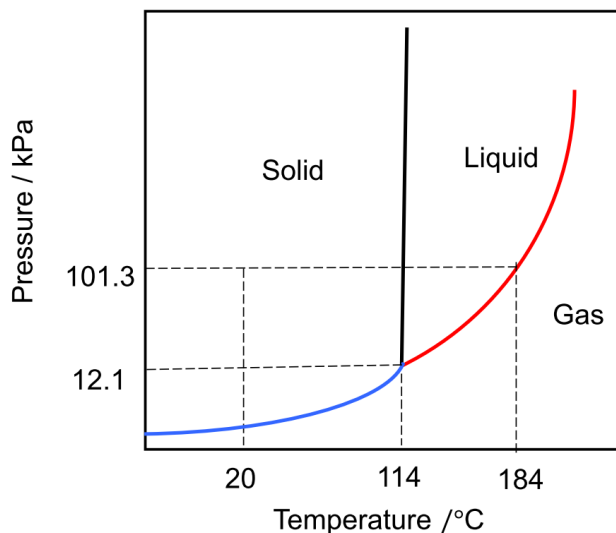


Figure 2. Phase diagram of iodine (modified from Reference 2)

3. Unit Lattice Models of Metal Crystals

In “Basic Chemistry” or advanced “Chemistry” courses, students learn two basic models of unit cells of metal crystals: body-centered cubic (bcc) and face-centered cubic lattice (fcc). The topic of this section is aimed at understanding the filling factor and coordination number. To aid student understanding, we use Styrofoam models. However, it is difficult to cut a Styrofoam sphere manually and precisely with a cutter knife into 1/2, 1/4, and 1/8 pieces. Using a conventional cutter knife, a

Styrofoam cutter that heats and melts by a nichrome wire, the cross section usually becomes uneven. The textbook also introduces a method of using a cutter knife to cut the sphere in one stroke.³ In many cases based on my experience, these activities fail to achieve the objectives to understand the arrangement of atoms in the unit lattice. Our school purchased commercially available Styrofoam models (**Figure 3**) for students to observe.



Figure 3. Commercial models of bcc and fcc lattices (Courtesy of NaRiKa Co.)

Recently, a conventional method has emerged for cutting Styrofoam accurately and easily.⁴ As a jig, a plaster mold is manually prepared to fit half of the sphere of Styrofoam. The plaster surface is then smoothed by sandpaper. Simply sliding a cutter along the surface gives one-half of a sphere with a smooth cut surface.

The cut spheres fit closely into a cubic acrylic box that is available at a 100-yen store. The benefits of this method are that it is reproducible and inexpensive. However, the teacher's working time to prepare the experiment is considerable.

4. Is NaCl Aqueous Solution Basic?

A normal salt is a salt in which neither H (acidic) nor OH (basic) remains in the substance. There is an experiment to determine rules of pH of salts based on the strength of the original acid and base. Three types of

salts are used in combination with the acid-base strength, such as sodium chloride, ammonium chloride, and sodium acetate.

Table 1. Properties of aqueous solutions of normal salts

| Normal Salt | Acid | Base | Property |
|-----------------------|----------------------------------|-----------------------------|----------|
| NaCl | HCl (strong acid) | NaOH (strong base) | ? |
| NH ₄ Cl | HCl (strong acid) | NH ₃ (weak base) | Acidic |
| CH ₃ COONa | CH ₃ COOH (weak acid) | NaOH (strong base) | Basic |

When we use reagent-grade sodium chloride, its solution is neutral (green by addition of the indicator BTB (bromothymol blue) solution). However, if "table salt" is used instead, its aqueous solution becomes basic (blue by

BTB solution). The reason is because table salt contains basic magnesium carbonate as an anti-sticking agent.

This experiment shows the importance of preliminary experiments and the use of appropriate substances.

5. Conclusion

We use various kinds of reagents and equipment in chemical experiments in senior high school. Experimental techniques should be easy for students to understand. However, it is difficult for instructors to find the technical

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information suitable for their classes in authorized databases such as SciFinder®. Teachers/instructors should catch up with innovative experimental techniques not only from the literature but from other sources.

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Author Information



Hiroyuki Onuki

He graduated the University of Tokyo in 1989 and received his Ph.D. degree from Graduate School of the University of Tokyo in 1994. He has worked in Nippon Suisan Kaisha, Ltd., RIKEN, Tokyo Chemical Industry Co., Ltd. and Junten Junior and Senior High School. He has concurrently served as an adjunct lecturer in Tokyo University of Agriculture and Technology, Tokyo Denki University, Graduate School of Yokohama City University, Rikkyo University, and Nihon University. In 2020, he was appointed as a science teacher in Toyo University Keihoku Senior High School.

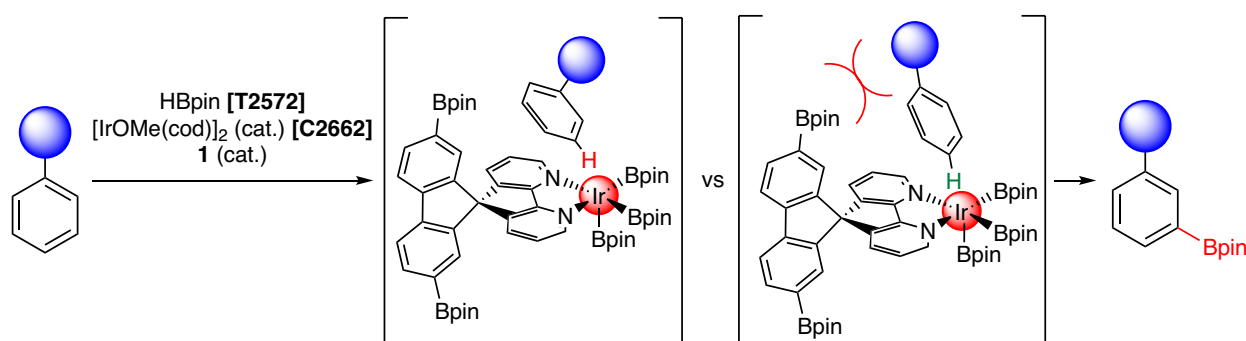
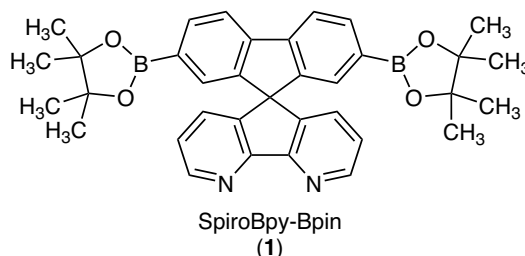
His research interests are organic natural product chemistry, instrumental analyses, and chemical education.

New Products Information

SpiroBpy-BPin: Ligand for *meta*-Selective Catalytic C-H Borylation



SpiroBpy-Bpin (1)

Product Number: **B6552****100mg 500mg**

Since the development of the C-H borylation reaction, which allows the introduction of a boron functional group directly onto the C-H of an arene, the variety of available borylated arenes has increased dramatically. In the early C-H borylation reactions, boron was introduced at sterically vacant positions of substituted arenes. *ortho*-Selective C-H borylation reactions using arenes having directing substituents, and *para*-selective borylation reactions using high sterically hindered ligands have been developed. However, it has not been easy to discriminate *meta*- and *para*-positions in the C-H borylation reaction for simple substituted arenes. Therefore, there is a need to develop ligands that exhibit *meta*-selectivity for a wide range of arenes.

SpiroBpy-Bpin (1) is a catalytic C-H borylation ligand that exhibits excellent *meta*-selectivity.^{1,2)} The Bpin substituent on the spirobipyridine moiety of 1 plays the role of a roof, and the *meta*-position of hydrogen of the substrate preferentially approaches the metal center, resulting in *meta*-selectivity. For example, in the C-H borylation of *tert*-butylbenzene using HBpin, [IrOMe(cod)]₂ and 1, the *meta*-selectivity reaches *m:p* = 23:1. A *meta*-selectivity of *m:p* = 5.0:1 is achieved even when the substrate is toluene. Thus, 1 shows excellent *meta*-selectivity for various substituted arenes, and the application of *meta*-borylated arenes is expected in the future.

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Related Products

(1,5-Cyclooctadiene)(methoxy)iridium(I) Dimer (= [IrOMe(cod)]₂)
Pinacol Borane
2,2'-Bis[bis(3,5-dimethylphenyl)phosphino]-1,1'-biphenyl

| | | |
|-------|-------|-------|
| 200mg | 1g | C2662 |
| 5g | 25g | T2572 |
| 100mg | 500mg | B5957 |

Anti-Non-human Glycoform Antibodies for Flow Cytometry



Anti- α Gal Polyclonal Antibody R-PE Conjugate (1)

Product Number: **A3354**
1VIAL

Anti-NeuGc Polyclonal Antibody R-PE Conjugate (2)

Product Number: **A3360**
1VIAL

Non-human glycoforms are known to trigger immune reactions in humans.^{1,2)} At TCI, we have developed a plethora of chicken polyclonal antibodies against such glycoforms, including the α Gal epitope (Gal α 1-3Gal) and N-glycolylneuraminic acid (Neu5Gc), in order to aid in their rapid, detection. **1** and **2** are anti-non-human glycoform antibodies conjugated with R-Phycoerythrin (R-PE) for use in flow cytometry, enabling the specific detection of such non-human glycoforms on the cell surface.

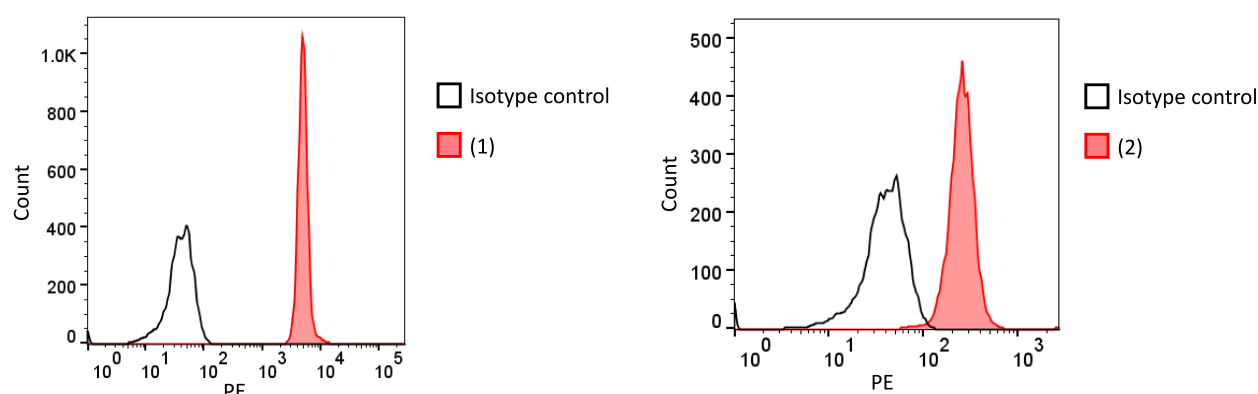


Figure. Detection of non-human glycoforms in porcine peripheral blood granulocytes

Peripheral blood cells were collected from miniature pig blood. **1**, **2** and an isotype control were prepared at a concentration of 0.01 mg/mL and incubated with cells for 20 min at 4 °C. Subsequent analysis of samples was performed on a flow cytometer.

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Related Products

| | | |
|--|-------|-------|
| Anti- α Gal Polyclonal Antibody (Chicken) | 1VIAL | A3123 |
| Anti- α Gal Polyclonal Antibody HRP Conjugate | 1VIAL | A3195 |
| Anti-NeuGc Chicken Polyclonal Antibody | 1VIAL | A3240 |
| Anti-NeuGc Polyclonal Antibody HRP Conjugate | 1VIAL | A3397 |

Xanthine Oxidase Inhibitor - Febuxostat



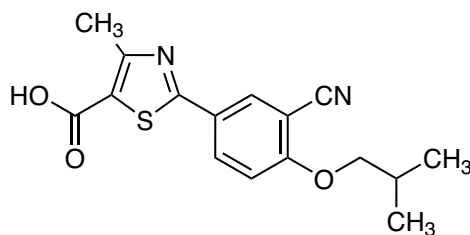
Febuxostat (1)

Product Number: **F0847**

1g 5g

Febuxostat (**1**) is known as an inhibitor of xanthine oxidase. Xanthine oxidase is involved in the conversion of xanthine to uric acid. By inhibiting this enzyme, **1** reduces the production of uric acid.¹⁾

Recently, **1** has been reported to suppress NLR family pyrin domain-containing protein 3 (NLRP3) inflammasome-mediated IL-1 β secretion and may be applied in related research studies.²⁾



Febuxostat
(**1**)

References

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Related Products

| | | | | |
|-----------|-----|------|------|-------|
| Xanthine | | | 25g | X0004 |
| Uric Acid | 25g | 100g | 500g | U0018 |

OCT4 Activators

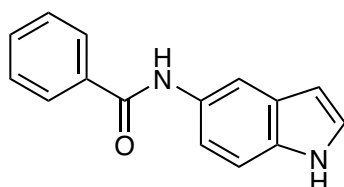


OAC-2 (1)

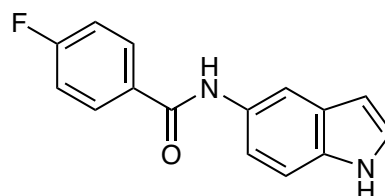
Product Number: **O0619**
25mg

OAC-3 (2)

Product Number: **O0614**
25mg



OAC-2
(1)



OAC-3
(2)

OCT4 is a master regulator of the induction and maintenance of cellular pluripotency, and has crucial roles in early stages of cell differentiation.¹⁾ OAC-2 (1) and OAC-3 (2) activate expression of OCT4.²⁾ These OCT4-activating compounds were identified using high-throughput screening by Li *et al.* and were found to enhance reprogramming efficiency from embryonic fibroblasts to induced pluripotent stem cells (iPSCs).

References

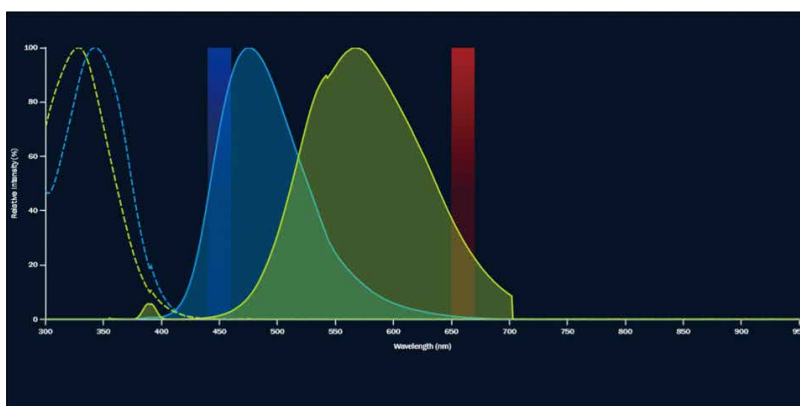
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Related Product

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| OAC-1 | 10mg | 50mg | O0490 |
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| <input checked="" type="checkbox"/> | Dansylsarcosine Cyclohexylammonium Salt (for i | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | Filter Name | 660 nm | 20 nm X |

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