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**Design of Porous Coordination Materials with Dynamic Properties**
Nobuhiko Hosono
Keywords: Liquid crystal | Supramolecular material | Self-assembly

Supramolecular Association and Nanostructure Formation of Liquid Crystals and Polymers for New Functional Materials
Takashi Kato,* Monika Gupta, Daisuke Yamaguchi, Kian Ping Gan, and Masanari Nakayama
https://www.journal.csj.jp/doi/abs/10.1246/bcj.20200304

Keywords: Surface modification | Grafting | Layered materials

Nanoarchitectonics through Organic Modification of Oxide Based Layered Materials; Concepts, Methods and Functions
Chalunda (Baitong) Tirayaphanitchkul, Kamonnart (Jaa) Imwiset, and Makoto Ogawa*
https://www.journal.csj.jp/doi/abs/10.1246/bcj.20200310

We describe here our concepts and achievements for material science, which have been introduced through liquid-crystalline, polymer, and supramolecular chemistry. They have resulted in the development of new class of functional organic, polymer, and hybrid materials. These strategy and material designs lead to the formation of new dynamically functional materials, which exhibit properties of stimuli-responsiveness, photoluminescence, transport of charge, ions, and molecules, electro-optic responses and templates for self-organization. They have potentials in the fields of energy, environment, healthcare, and bioscience as well as advanced technologies.

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Grafting reactions for the surface modification of metal oxide based nanomaterials are summarized with the emphasis on layered solids. The fundamentals (the character of the nanomaterials and the experimental procedures) are introduced followed by the nanoarchitectures of the products, which are classified in order to clarify the present status on the nanoarchitecture design.
Keywords: Organic photovoltaics | Vacuum process | Small molecule OPV

Small Molecules for Vacuum-Processed Organic Photovoltaics: Past, Current Status, and Prospect
Addanki Venkateswararao and Ken-Tsung Wong*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200330

Keywords: Fluorescence | Nucleic acid | Biosensor

Fluorescent Nucleic Acid Systems for Biosensors
Arup Podder, Ha Jung Lee, and Byeang Hyean Kim*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200351

Vacuum-processable small-molecule materials are collected and categorized into several sub-groups based on the arrangements of donor and acceptor units. In each category, the structure-property-molecular interaction-performance relationship is discussed. Challenges and important prospects for future inventions of small-molecule materials are proposed to obtain vacuum-processed OPV devices with better performance for commercialization.

Keywords: Fluorescence | Nucleic acid | Biosensor

Fluorescence-based nucleic acid systems have been studied extensively for their implementation in molecular biology as platforms for disease diagnosis. In this Account, we discuss the study of single-nucleotide polymorphisms, duplex DNA, pH-dependent oligodeoxynucleotides (ODNs), i-motifs, G-quadruplexes, trinucleotide repeats, quencher-free molecular beacons, and three-way junction-based ODN systems through fluorescence phenomena, and their applications in specific areas.
This article reviews the synthesis strategies for monolayer COFs on solid substrates and interface synthesis methods for COF thin films with controlled thickness, uniform morphology and promising crystallinity. Film-form COFs are beneficial to realize applications of COFs in many fields such as optoelectronic devices, electronic devices, electrocatalysis and molecular separation.

**Keywords:** Fullerene | Carbon nanotubes | Organic solar cells

**Creation of Highly Efficient and Durable Organic and Perovskite Solar Cells Using Nanocarbon Materials**

Yutaka Matsuo  

Research approaching carbon-rich solar cells using nanocarbon material components is described. Doped carbon nanotubes transparent electrodes, fullerene derivative electron transporters/passivators, and endohedral fullerenes dopant in organic and perovskite solar cells are discussed for high performance and stability of solar cells.

**Keywords:** Covalent organic framework (COF) | Interface synthesis | Thin film

**Synthesis of Covalent Organic Framework Films at Interfaces**

Bin Bai, Dong Wang, and Li-Jun Wan*  
Keywords: Cr(VI) removal | Photocatalytic reduction | Photocatalyst

Research Progress on Photocatalytic Reduction of Cr(VI) in Polluted Water
Gaoqian Yuan, Faliang Li,* Kezhuo Li, Jie Liu, Junyi Li, Shaowei Zhang, Quanli Jia, and Haijun Zhang*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200317

Different methods about the removal of toxic Cr(VI) were introduced and the effects of photocatalysts structure on their photocatalytic Cr(VI) reduction performance were emphasized.

Keywords: Covalent organic frameworks | Two-dimensional polymers | Design and synthesis

Donglin Jiang
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200389

This award account trailed our way toward and showed our initiatives of covalent organic frameworks, the exploration of design principle and synthetic strategies, and the development of functions and properties. By elucidating various interplays, we scrutinized the unique features of materials and the origins of different functions.
A Review on the Synthesis and Applications of Nanoporous Carbons for the Removal of Complex Chemical Contaminants

Gurwinder Singh, Jang Mee Lee, Gopalakrishnan Kothandam, Thavamani Palanisami, Al'a H. Al-Muhtaseb, Ajay Karakoti, Jiabao Yi, Nanthi Bolan, and Ajayan Vinu*

https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200379

The review encompasses a summary of the latest developments in the field of synthesis of nanoporous carbon-based materials from various precursors including biomass, coal and others. The crucial parameters required for good adsorption properties are highlighted. From an application point of view, the use of these materials for the removal of inorganic, organic and radioactive contaminants are discussed.

Controlled Nanostructures Fabricated by the Self-Assembly of Gold Nanoparticles via Simple Surface Modifications

Hideyuki Mitomo and Kuniharu Ijiro*

https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210031

Fabrication of sophisticated metal nanostructures has attracted much attention. In this review, we introduce recent advances in the fabrication of metal nanostructures via self-assembly with a particular focus on our studies, in which AuNPs are modified with oligo(ethylene glycol) (OEG)-terminated alkane thiol derivatives as simple small molecules with definite structures.
**Keywords:** Singlet-to-triplet absorption | Triplet-triplet annihilation | Photon upconversion

**Singlet-to-Triplet Absorption for Near-Infrared-to-Visible Photon Upconversion**

Yoichi Sasaki, Shogo Amemori, Nobuhiro Yanai,* and Nobuo Kimizuka*


This review highlights the recent advancement of singlet-to-triplet (S–T) absorption for triplet-triplet annihilation-based photon upconversion (TTA-UC) from near-infrared (NIR) light to yellow, blue, and even violet light. Taking advantage of the molecular donor's ability to be dispersed in solids without aggregation, the efficient solid-state NIR-to-visible TTA-UC is also achieved.

**Keywords:** Alkyl-fullerene hydrophobic amphiphile | Fine-tuning of self-assembly | Optoelectronic devices

**Alkyl-Fullerene Materials of Tunable Morphology and Function**

Edward A. Neal and Takashi Nakanishi*


The attachment of alkyl chains to fullerene cores produces alkyl-fullerene hydrophobic amphiphiles that undergo self-assembly, with retention of fullerene electrochemical and optoelectronic functions. Chain length, substitution position and branching variation afford lipid bilayer electrodes, lamellar nanowires and micellar structures, but also unusual kinetically assembled solid objects and room-temperature liquids in which the alkyl chains isolate the fullerene cores.
Layer-by-layer methods are useful for constructing polymeric materials by exploiting weak interactions such as van der Waals interactions and protein affinity. Using these scientific techniques, we have successfully developed template polymerization for synthesis of stereoregular polymers, dramatic morphology control of nanomaterials, and three-dimensional (3D) cellular tissue models.

This review systematically classifies the emerging metal-iodine/bromine batteries including Zn-I$_2$ and Zn-Br$_2$ batteries, Li-I$_2$ and Li-BrCl batteries and other metal-I$_2$ batteries. We summarize the state-of-the-art progress of energy storage mechanisms and discusses the main issues currently. Furthermore, some promising solutions proposed during the past few years are highlighted to outline key perspectives for future research in this thriving field.
In this Account, we highlight our recent studies on the encapsulation of polymer chains into metal–organic frameworks (MOFs), which provides a powerful tool for synthesizing functional materials. Introducing polymers into the MOF nanochannels renders unprecedented forms of hybrid materials that exhibit many nanoscale functions. In addition, the regular nanoporous structure of MOFs enables the recognition of the polymer structure, providing a new separation technology for macromolecules.

A majority of the biological tissues have well-defined anisotropic structures and exhibit a range of biological, mechanical, and other functions that support survival. In this account, we summarize the progress in anisotropic hydrogels having unidirectional alignments of lamellar bilayers, mainly focusing on biologically inspired layered structures, fabrication strategies, and interesting anisotropic properties, including one-dimensional swelling, anisotropic diffusion, photonic properties and specific mechanical properties.
This Account summarizes our recent research progress on gels composed of self-assembled cello-oligosaccharide networks, from production to applications. In contrast to ordinary assembled molecular gels with dynamic properties, these cello-oligosaccharide gels are static and highly robust. Our findings suggest that statically assembled molecular gels have unconventional applications.

In this mini-review, we discuss the preparation of molecular scale one-dimensional (1D) channels by using non-covalent interactions and covalent bonds between pillar[n]arenes. Connecting both pillar[n]arene rims via physical interactions or covalent bonds, enables preparation of continuous and discrete 1D channels. Non-covalent 1D channels can also be produced by complexation between pillar[n]arene wheels and polymeric axles.
This account article summarized global trends in waste plastic recycling, feedstock recycling through pyrolysis-based approaches for hard-to-recycle plastic wastes, and the applicability of pyrolysis-gas chromatography (Py-GC) for investigating the pyrolysis reaction mechanism, in situ pyrolyzate monitoring, and rapid screening of pyrolysis and catalytic reaction conditions.

Data-scientific approach has potential for acceleration of our research. However, the application to small data, such as experimental data, is a current challenge. This account shows materials informatics for 2D materials, as a model case. Combination of sparse modeling and chemical perspective provides straightforward, accessible, and interpretable prediction models for design of materials, optimization of processes, and enhancement of performance.
The science of electrode processes will be a key to provide the game-changing technology towards the ongoing challenges related to carbon neutrality, however, further advancements of fundamental concepts and theories of electrode process are indispensable for both solid-state and surface systems. This account summarizes several attempts to acquire further understanding on fundamental and microscopic aspects of these electrode process.

A phase transition transistor has been realized by using an organic Mott insulator. Both electric field effect and strain effect can induce insulator-to-metal and superconducting transitions by bandfilling control and bandwidth control, respectively. The measurement results have uncovered an unknown phase diagram of the strongly correlated electron system where temperature, density, and kinetic energy of electrons play important roles.
In this account, we briefly introduce our recent studies on novel single-component molecular conductors based on multi-orbital correlated π-d electron system \([M(tmdt)_2]\) (M = Ni, Pd, Pt, Cu and Au), the first single-component molecular superconductor \([Ni(hfdt)_2]\), and the nodal-line Dirac electron system \([M(dmdt)_2]\) (M = Pt and Ni).

Oriented MOF thin films were fabricated via heteroepitaxial growth on metal hydroxides. All three crystallographic alignments were achieved when the lattice-matching conditions fulfilled the requirements. Oriented MOF films are expected to be used in a variety of sophisticated applications such as electronics, photonics, and magnetics via the host–guest approach for the enhanced functionalities.
Synthesizing MOFs using ambient conditions is of interest to meet the demands of sustainable chemistry as well as to enlarge function tunability. MOFs prepared at room temperature are summarized in this review with a particular emphasis on chemically stable MOFs and related composites, including their synthesis strategies and emerging properties.

We describe here the dynamic and static memory of the macromolecular helicity that we have developed during the past two decades. The helical polymers with dynamic and static helicity memory have been proven to be exceptionally unique, leading to the development of novel advanced chiral materials with specific functions that may not be realized by synthetic and biological helical systems.
**Keywords:** Metal-organic frameworks (MOFs) | Inverse adsorption | CO$_2$/C$_2$H$_2$ separation

**An Ultramicroporous Metal-Organic Framework with Record High Selectivity for Inverse CO$_2$/C$_2$H$_2$ Separation**

Hui Cui, Yi Xie, Yingxiang Ye, Yanshu Shi, Bin Liang,* and Banglin Chen*


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210237

An ultramicroporous Metal-Organic Frameworks (MOFs) composed of Cu(II) ions and 4,4′-(hexafluoroisopropylidene) bis(benzoic acid) linkers forming two-fold interpenetration gives an overall three-dimensional network featuring 1D zigzag pore channels. This MOF shows inverse adsorption of carbon dioxide over acetylene with a much higher CO$_2$/C$_2$H$_2$ uptake ratio and high CO$_2$/C$_2$H$_2$ selectivity.

**Keywords:** Ionic liquid | Polymer electrolyte | Soft matter

**Advances in Organic Ionic Materials Based on Ionic Liquids and Polymers**

Masayoshi Watanabe


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210281

Significant contributions to the development of organic ionic materials based on ionic liquids and polymers have been discussed and reviewed in this paper. A detailed investigation of the ion dynamics in these materials and their interfaces with electrodes has led to the development of the field of organic ionics. Furthermore, unique stimuli-responsive smart materials based on ionic materials have been developed.
**Keywords:** Persistent luminescence | Lanthanoid ion | Electron trap

**How to Design and Analyze Persistent Phosphors?**
Jumpei Ueda


Until now persistent phosphors have been developed through the trial-and-error experimental procedure. In this study, we successfully develop the persistent phosphors based on the design guide using vacuum referred binding energy diagram.

**Keywords:** Designer materials | Noble carbons | Nanoarchitecture

**Carbonaceous Materials: The Beauty of Simplicity**
Nieves López-Salas and Markus Antonietti*


Materials chemistry should be redesigned to minimize wastes and side products. Carbon-based chemistry is among the most versatile when discussing materials sciences. But, redesign it and, at the same time, outperforming other materials is still challenging. Herein, we give our critical opinion on the different strategies new generation scientists should use to achieve such a goal.
**Electrochemical Sensing Applications Using Diamond Microelectrodes**  
Tribidasari A. Ivandini and Yasuaki Einaga*  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210296  

Fabrication and characterization of boron-doped diamond (BDD) microelectrodes especially in the form of micro needle electrodes are described. They showed not only more extreme lower background current than diamond macroelectrode, but also an ability for analytical sensing in low conductive media. Here, wider range of experiments including in vivo measurements could be performed.

**Supported, ~1-nm-Sized Platinum Clusters: Controlled Preparation and Enhanced Catalytic Activity**  
Tokuhisa Kawawaki, Nobuyuki Shimizu, Yusuke Mitomi, Daichi Yazaki, Sakiat Hossain, and Yuichi Negishi*  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210311  

This account describes our previous studies on 1) the synthesis of ligand-protected ~1-nm-sized platinum (Pt) clusters, 2) the preparation of supported ~1-nm-sized Pt clusters, and 3) the catalytic activity of the catalysts obtained for carbon monoxide/hydrocarbon oxidations and for the oxidation reduction reaction, which were conducted to contribute to the reduction of Pt use in our future society.
The sciences on naturally occurring circular DNA/RNA and artificially synthesized ones are rapidly growing, and their interdisciplinary areas are highly promising for future applications.

Cytochrome $c$ transfers electrons in the respiratory chain and also triggers apoptosis. We found the following aspects of cytochrome $c$: It forms oligomers and polymers by 3D domain swapping. It has a relatively wide membrane interaction site, recognizing lipids and partner proteins in a similar way. Met80 is oxidized to methionine sulfoxide with $\text{H}_2\text{O}_2$ or $\text{O}_2$, enhancing the peroxidase activity.
This account describes our work concerning the application of alkylboranes to addition reactions to unsaturated compounds, with catalysis by copper. Alkylboranes are readily obtained from standard alkene hydroboration reactions, which is an advantage of these processes. The substrates can contain a wide range of functional groups. The reactions described herein include the formation of alkylcopper(I) species via the catalytic B/Cu transmetallation of alkylboranes and subsequent addition to unsaturated carbon–carbon bonds or carbon dioxide.

Metal homoenolates represent uniquely useful organometallic intermediates, allowing umpolung synthesis of β-functionalized carbonyl compounds. Unprotected cyclopropanols have emerged as attractive precursors to metal homoenolates, often catalytically generated, in carbon–carbon and carbon–heteroatom bond-forming reactions. This review provides an overview of the development of such homoenolate transformations, as classified with respect to the metals involved in the cyclopropane ring opening.
The planar trigonal structure of 1,3,5-trisubstituted benzene, named phenine, has been adopted as basic units of polygonal networks to shape nanometer-sized curved organic π-molecules. The phenine design allows for concise syntheses of large carbonaceous molecules reaching 4 kDa by stitching geodesic lines with aryl coupling reactions. In this Account, the development of the defective nanocarbon molecules, i.e., geodesic phenine frameworks, is summarized to overview unique structural/electronic features.

This account describes a series of urea/thiourea based receptors for the detection and differentiation of fluoride, cyanide, and tabun. First, our journey begins with development of novel chromo-fluorogenic probes for the specific detection of fluoride and cyanide anions. Finally, the developed knowledge was implemented on nerve agent detection. Urea/thiourea motifs have been extensively used in the chemosensing of anionic and neutral analytes, supramolecular catalysis, and supramolecular medicinal chemistry. Here, these aspects have also been briefly summarized.
We summarize our recent results in the design and application of metal complexes bearing $N$-phosphine-oxide-substituted imidazolylidenes (PoxIms), which can drastically change the spatial environment around the carbene atoms through the rotation of their $N$-phosphinoyl groups. These results have expanded the frontiers of multifunctional $N$-heterocyclic carbenes beyond their traditional use as multidentate ligands for metal complexes.

We summarized our recent efforts to develop molecular transformations utilizing organosuperbase catalysts, which include the carbon-carbon bond formations involving the generation of carbanions of less acidic compounds through the formal umpolung process from carbonyl compounds and the formal [3+2] cycloadditions involving the generation of the synthetic equivalent of a 1,3-dipole through the epoxide opening.
The aim of this review is to summarize the progress made thus far in the development of artificial metalloenzymes (ArMs). Besides summarizing the major types of ArMs in literature, a focal point of emphasis will highlight how groups worldwide are beginning to adapt their molecular selectivity to areas of pharmaceutical synthesis, diagnostics, and drug therapy.

This account describes our journey in controlling the reactivity of organoiron species, and developing an iron catalyst that can efficiently activate a C–H bond, followed by reaction with nucleophiles, electrophiles, or with another C–H substrate. Forays into C–H activation using cobalt, manganese, and chromium catalysis are also briefly presented.
**Keywords:** Thorpe-Ingold effect | Polymer conformation | Photophysical properties

Thorpe-Ingold Effect on Polymer Conformations. Photophysical Behavior as a Probe for Folding of *Alt*-Dialkylsilylene-divinylarene Copolymers
Tien-Yau Luh,* Chih-Hsien Chen,* and Guo-Qiao Lai*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200289

The *alt*-silylene-conjugated motif copolymers consist of donor and acceptor chromophores regioselectively arranged in alternating manner and the two adjacent chromophores are linked by a tetrahedral dialkylsilylene insulating spacer. These polymers are highly folded, and the bulkier isopropyl group on silicon may exert Thorpe-Ingold effect that can bring the adjacent chromophores to closer proximity resulting in changing photophysical properties.

**Keywords:** Alkylsilyl peroxides | Alkyl radicals | β-Scission

Development of Organosilicon Peroxides as Practical Alkyl Radical Precursors and Their Applications to Transition Metal Catalysis
Akira Matsumoto* and Keiji Maruoka*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200321

Efficient methods for the generation of alkyl radicals from structurally diverse organosilicon peroxides have been developed. In the presence of a suitable transition metal catalyst, various alkyl radicals can be generated under mild reaction conditions, which have been successfully involved in the formation of carbon–carbon and carbon–heteroatom bonds to construct functionalized carbon skeletons in chemoselective or asymmetric manners.
Keywords: Trifluoromethylation | Heteroaromatic compound | Regioselective

Regioselective C-H Trifluoromethylation of Heteroaromatic Compounds
Yoichiro Kuninobu* and Takeru Torigoe
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200302

Regioselective C-H trifluoromethylation of heteroaromatic compounds are summarized. This review article consists of four sections: (1) Introduction; (2) C-H trifluoromethylation of five-membered heteroaromatic compounds; (3) C-H trifluoromethylation of six-membered heteroaromatic compounds; and (4) Conclusion. Each section is categorized by the reaction sites.

Keywords: Foldamer peptides | Cyclic amino acids | Ribosomal synthesis

Development of Bioactive Foldamers Using Ribosomally Synthesized Nonstandard Peptide Libraries
Takayuki Katoh* and Hiroaki Suga*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200326

Development of a novel designer tRNA, tRNA\textsuperscript{Pro1E2}, enabled the ribosomal incorporation of D-, β-, and γ-amino acids into peptides. A foldamer peptide library containing three types of cyclic β-amino acids as strong turn/helix inducers was applied to the screening of FXIIa inhibitors, by which we successfully obtained a potent FXIIa inhibitor, F3, that forms an anti-parallel β-sheet structure.
Keywords: Chirality | Selectivity | Symmetry
Symmetry as a Tool for Solving Chemical Problems
Christina Moberg
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200338

An object — such as a sculpture, a building, a molecule — which is invariant with respect to reflection or rotation, or a combination of the two, possesses some kind of symmetry. But real molecules are never motionless — they constantly change their conformations — and so do people.

Keywords: Perovskite solar cells | Hole transporting materials | Pyrene
Pyrene-Cored Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells
Jiang-Yang Shao and Yu-Wu Zhong*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200331

The recent advances of organic hole-transporting materials (HTMs) with a pyrene backbone for efficient and stable perovskite solar cells (PSCs) are discussed, including small molecular HTMs, electropolymerized films as dopant-free HTMs, and a pyrene-cored sulfur-rich molecule as an interfacial layer of PSCs.
Recent advancements in enantioselective direct C–H addition to carbonyls and Michael acceptors are highlighted. These enantioselective C–H additions, catalyzed by Ir, Rh, and Co catalysts, provide a straightforward access to structurally diverse and valuable chiral fragments.

Some winding roads towards an “iron age” are discussed, as traveled in the author’s laboratory. This includes efforts to emulate conventional cross coupling chemistry with cheap iron salts, and searches for novel iron catalyzed transformations such as ring-opening/cross coupling of heterocycles, the formation of internal alkynes from lactones, unorthodox cycloisomerizations, and a case study in C–H activation.
Organocatalysis provides cooperative actions of multiple mild activations, which are essential even in intrinsically rapid organic reactions. The enzyme-like catalytic system is effective for recognizing specific molecular conformations of substrates through multipoint interactions, thereby leading to high stereoselectivity. On the basis of this concept, we developed various organocatalytic asymmetric synthetic reactions, which are challenging using other categories of catalysts.

Inspired by nature’s prowess at the biosynthesis of structurally ornate organic molecules, this review provides a personal perspective of a three-decade journey directed at the efficient aldol-based total synthesis of a selection of complex polyketide natural products completed in our group.
Keywords: Catalytic | Enantioselective | Proton transfer
Catalytic Enantioselective Proton Transfer Reactions
Jin Cao and Shou-Fei Zhu*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200350

Enantioselective proton transfer can easily construct tertiary carbon stereocenters but remains a long-lasting challenge in asymmetric synthesis. This paper reviews the recent progress on catalytic enantioselective proton transfer reactions according reaction types, classifying the stereocontrol strategies of catalytic proton transfer, and presents prospects of this field.

Keywords: Carbon | Allotrope | Polyyne
A Short History of Cyclocarbons
Harry L. Anderson,* Connor W. Patrick, Lorel M. Scriven, and Steffen L. Woltering
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200345

The cyclocarbons constitute a family of molecular carbon allotropes consisting of rings of two-coordinate atoms. Their high reactivities make them difficult to study, but there has been much progress towards understanding their structures and properties. Here we provide a short account of theoretical and experimental work on these carbon rings, and highlight opportunities for future research in this field.
Keywords: Phthalocyanines | Near-infrared | Circularly polarized luminescence

Development of Phthalocyanine-Based Functional Molecules with Tunable Optical and Chiroptical Properties
Atsuya Muranaka* and Masanobu Uchiyama*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200336

Phthalocyanines and related compounds are of both fundamental and practical interest because of their unusual physical properties arising from the presence of extended π-conjugation systems, and they have a wide range of applications from conventional dyes and pigments to advanced functional materials. In this account, we briefly introduce our work on the development of phthalocyanine-based functional molecules exhibiting near-infrared (NIR) absorption or circularly polarized luminescence (CPL).

Keywords: o-Carborane | Boron | B-H functionalization

Recent Advances in Transition Metal-Catalyzed Selective B-H Functionalization of o-Carboranes
Yik Ki Au and Zuowei Xie*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200366

This review summarizes and discusses recent advances in transition metal catalyzed regioselective B-H functionalization of o-carboranes using a general strategy with three rules: (1) employing electron-rich transition metal catalysts for B(3,6)–H functionalization; (2) utilizing electrophilic transition metal catalysts for B(8,9,10,12)-H functionalization; and (3) merging directing groups with electrophilic transition metal catalysts for B(4,5,7,11)–H functionalization.
This Account discusses for the first time helical self-organizations and their emerging functions starting from artwork such as architectural monuments to biological macromolecules and their complexes and to synthetic supramolecular and covalent macromolecules and their complexes. Historical developments for all these classes of helical self-organizations are discussed. The current limitations of synthetic helical self-organizations are also discussed.

One-shot and one-pot borylation reactions based on the tandem bora-Friedel–Crafts reactions (electrophilic C–H borylation of arenes) are summarized. The reactions take place with an appropriate choice of boron source, Lewis acid, Brønsted base, and reaction temperature, to construct polycyclic frameworks with ring junction boron atoms. The borylated compounds exhibit attractive optoelectronic properties and substantial stabilities in practical applications.
Keywords: Alkaloids | Radicals | Rearrangement

Total Synthesis of Talatisamine: Exploration of Convergent Synthetic Strategies
Tsukasa Shimakawa, Koichi Hagiwara, and Masayuki Inoue*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200400

Talatisamine (1) is a highly oxygenated C_{19}-diterpenoid alkaloid, with K^+ channel inhibitory, antiarrhythmic, and neuroprotective activities. Its intricately fused 6/7/5/6/6/5-membered hexacyclic structure (ABCDEF-ring) possesses one nitrogen functionality, five oxygen functionalities, and 12 contiguously aligned stereocenters. This account describes the development of convergent strategies to efficiently assemble this synthetically challenging natural product.

Keywords: Carbon dioxide | 1,3-Butadiene | Copolymerization

New Polymers Made from Carbon Dioxide and Alkenes
Kyoko Nozaki
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200402

Carbon dioxide (CO_{2}) is an attractive raw material for chemical synthesis owing to its abundance and low toxicity. Among various utilization of CO_{2} for the synthesis of useful compounds, this article focuses its use for polymer synthesis, especially using a lactone derived from CO_{2} and 1,3-butadiene.
Liquid-liquid phase separation (LLPS) of proteins and RNAs in living organisms is a recently emerging biologic infrastructure that leads to various functions and disfunctions. Here, we introduce the basic biology of LLPS and present challenges in the field from a chemical viewpoint.

Radical-based cross-coupling reactions are powerful tools to construct congested C(sp³)–C(sp³) bonds. In this review, we highlight persistent tertiary carbon radicals generated from carbonyl or related compounds, with emphasis on the role of the dimer/radical equilibrium. We summarize the historical background and present selected recent examples of these cross-coupling reactions, grouped according to the originally proposed mode of bond formation.
**Keywords:** Gold catalysis | Chloride scavenging | Au(I) chloride complexes

**Silver-Free Catalysis with Gold(I) Chloride Complexes**

Allegra Franchino, Marc Montesinos-Magraner, and Antonio M. Echavarren*


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200358

This review describes recent advances in the field of silver-free Au(I) catalysis employing gold(I) chloride complexes, with an emphasis on approaches emerged in the last decade. Both the development of alternative chloride scavengers and the design of self-activating gold(I) chloride complexes endowed with special ligands are discussed in detail.

**Iron-Catalyzed Cross-Coupling Reactions Tuned by Bulky Ortho-Phenylene Bisphosphine Ligands**

Laksmikanta Adak, Takuji Hatakeyama, and Masaharu Nakamura*


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200392

Iron-catalyzed protocols not only benefit from economic and toxicology standpoints, but also exhibit a range of reactivities and tolerate many functional groups. To date several iron catalyst systems have been developed, ranging from the use of simple iron salts to more complex stoichiometric/catalytic modifiers. This account summarizes the recent developments in iron-catalyzed cross-coupling reactions employing bulky o-phenylene bisphosphine ligands and their mechanistic views.
Keywords: Chalcogen-containing hole-transporting materials | Perovskite solar cells | Sulfur-containing cores

Chalcogen-Containing Hole Transporting Materials
Inés García-Benito, Javier Urieta-Mora, Agustín Molina-Ontoria, and Nazario Martín*

https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210032

Currently, there is no doubt that organic compounds are an important part of the PSCs architecture. This review summarizes our recent achievements in the development of new chalcogen-containing materials employed as HTMs in efficient PSCs. Therefore, our main goal is to contribute to a better understanding of the chemistry behind competitive HTMs and provide a clear picture of the effect of chalcogen-containing HTMs in device performances.

Keywords: Strained molecule | Hyper covalent bond | Hexaphenylethane

Expandability of the Covalent Bond: A New Facet Discovered in Extremely Long $C_{sp3}$-$C_{sp3}$ Single Bonds
Yusuke Ishigaki, Yasuto Uchimura, Takuya Shimajiri, and Takanori Suzuki*

https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200374

By the reductive ring closure of dicationic precursors, highly strained hexaphenylethanes with an extremely long C-C bond were obtained, in which the front strain among the aryl group is maximized with high eclipseness by fusing a ring structure. The fused ring also induces further bond elongation by scissor effect, which led us to discover the new feature of covalent bonds.
**Keywords:** SARS-CoV-2 | Mutation | ACE2

**Molecular-Level Anatomy of SARS-CoV-2 for the Battle against the COVID-19 Pandemic**
Makoto Komiyama

This account covers chemical information on COVID-19 with special emphasis on molecular-level understanding. Various features of SARS-CoV-2 (the infection mechanism, the effect of mutation on the infectivity, and others) are discussed in detail in terms of structural data.

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**Keywords:** Sumanene | Triazasumanene | π-Figuration

**The Dawn of Sumanene Chemistry: My Personal History with π-Figuration**
Hidehiro Sakurai

A personal history of sumanene chemistry: from the encounter with Prof. Mehta’s first report to the synthesis of pristine triazasumanene is described.
Recent developments on the design of PNA derivatives to recognize target sites in various forms of DNA and RNA are comprehensively surveyed. Chemical features of these DNA and RNA are notably altered at the target site, resulting in site-selective chemical transformations therein.

Nucleic acids store genetic information in canonical B-type double helices and direct biological functions through non-B-type highly-ordered structures. We described historical attempts, involving physicochemical analyses of structure and stability of nucleic acids, and our attempts to understand biological functions of nucleic acids, to explain underlying mechanisms based on their behaviors, considering that their dynamics depend on the surrounding molecular environment.
Modulation of Microtubule Properties and Functions by Encapsulation of Nanomaterials Using a Tau-Derived Peptide
Hiroshi Inaba* and Kazunori Matsuura*

https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210202

Microtubules (MTs) are fascinating cytoskeletons for cell manipulation and material applications. However, the study of the inside of MTs (15 nm inner diameter) is in its infancy. This account highlights our approach for encapsulation of nanomaterials inside MTs by using a Tau-derived peptide. Since the properties and functions of MTs are modulated by the encapsulation, molecular encapsulation is a new concept for understanding and modulation of MTs.

Polyketone-Based Molecular Ropes as Versatile Components for Functional Materials
Yasuhide Inokuma* and Yuya Inaba

https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210223

Polyketones are rope-like molecular components characterized by conformational flexibility and diversity in ketone-related reactions. Our recent research enabled access to stable discrete polyketones for use as versatile molecular components in functional materials. This account introduces the design and synthesis of polyketone-based prototype materials, such as solid-state fluorophores and metal-ion adsorbents, using a rope manipulation strategy.
**Keywords:** Organic radicals | Open-shell | Phenalenyl Syntheses and Properties of Open-Shell \(\pi\)-Conjugated Molecules  
Takashi Kubo  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210224

This account presents our recent studies on the investigation of the properties of organic radical species through a structural organic chemistry approach to synthesize molecules with new frameworks, particularly focusing on singlet biradical character of bisphenalenyl molecules, electron localization at zigzag edges of anthenes, and association behavior of phenalenyl radicals.

**Keywords:** \(\pi\)-Electronic ion pairs | Porphyrins | Supramolecular assemblies  
**Charged Porphyrins: \(\pi\)-Electronic Systems That Form Ion-Pairing Assembled Structures**  
Kazuhsa Yamasumi and Hiromitsu Maeda*  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210232

\(\pi\)-Electronic ions exhibit distinct assembling modes depending on the nonconventional interactions, \(\pi-\pi\) interactions, between charged \(\pi\)-electronic systems. We have adopted charged porphyrins as the components of ion-pairing assemblies because of their structural diversity and large \(\pi\)-systems to stabilize the charged states. This account focuses on the charged porphyrins and their ion-pairing assemblies.
Keywords: Boron | Near-infrared emission | Aza-substitution

Design Strategies and Recent Results for Near-Infrared-Emissive Materials Based on Element-Block $\pi$-Conjugated Polymers

Masayuki Gon, Shunichiro Ito, Kazuo Tanaka,* and Yoshiki Chujo*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210235

We summarize our molecular design strategies and recent results for preparing NIR-emissive materials based on element-block $\pi$-conjugated polymers. Taking advantage of inherent element properties, the energy levels of frontier molecular orbitals can be controlled by using aza-substitution and hypervalent bond, leading to narrowing energy gaps without expanding $\pi$-conjugated systems.

Keywords: Molecular self-assembly | The hydrophobic effect | Van der Waals interaction

Molecular “Hozo”: Thermally Stable Yet Conformationally Flexible Self-Assemblies Driven by Tight Molecular Meshing

Yi-Yang Zhan and Shuichi Hiraoka*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210228

Inspired by the traditional artisanal method, Hozo, for furniture making, a novel concept, termed molecular “Hozo” is presented to construct discrete molecular self-assembly through tight molecular meshing. Accordingly, we developed a series of water-soluble cube-shaped assemblies, nanocubes, driven by the hydrophobic effect, van der Waals and cation-$\pi$ interactions, from gear-shaped amphiphiles featuring large, indented complementary hydrophobic surfaces.
**Keywords:** Topology | Self-assembly | Folding

Orderly Entangled Nanostructures of Metal–Peptide Strands
Tomohisa Sawada* and Makoto Fujita
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210218

In this account review, we introduce our recent achievements in construction of highly entangled metal–peptide nanostructures based on a folding-and-assembly strategy. Starting from the initial design of the system, we discuss the remarkable examples such as polyhedral links, torus knots, and a polycatenane, and state perspectives.

**Keywords:** Supramolecular polymer | Polyrotaxane | Macroscopic self-assembly

Supramolecular Polymers and Materials Formed by Host-Guest Interactions
Akira Harada,* Yoshinori Takashima, Akihito Hashidzume, and Hiroyasu Yamaguchi
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210233

Supramolecular polymers and materials have been designed and prepared using macromolecular recognition by cyclodextrins as host parts. Polyrotaxanes, tubular polymers, supramolecular machines, artificial polymerases have been obtained by main-chain recognition. Macroscopic-self-assembly, self-healing materials, sol-gel transition, muscle-like materials have been achieved by side-chain recognition. End-group recognition leads to the construction of supramolecular polymers in narrow sense.
**Theoretical and Physical**

**Keywords:** Metal clusters | Catalysis | Polymer

Exploring Novel Catalysis Using Polymer-Stabilized Metal Clusters  
Shingo Hasegawa and Tatsuya Tsukuda* 
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200377

This article summarizes our recent works on the exploration of novel catalysis using polymer-stabilized metal clusters. The correlation between structural parameters and catalytic performances reported here will contribute to the development of the design principle for highly active and selective metal cluster catalysts.

**Keywords:** Dynamics | Molecular assembly | Physical response

Chemical Design and Physical Properties of Dynamic Molecular Assemblies  
Tomoyuki Akutagawa 
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200384

The thermally activated motional freedom of protons, ions, and molecules can be controlled using supramolecular approaches, which are combined with physical properties of proton conduction, ion conduction, dielectric switching, molecular rotator, collective rotation, ferroelectrics, molecular sorption, fluorescent chromism, and molecular sensing.
**Keywords:** Nonadiabatic electron dynamics | Beyond-Born-Oppenheimer chemistry | Multi-dimensional nonadiabatic interactions

**Electron Dynamics in Molecular Elementary Processes and Chemical Reactions**

Kazuo Takatsuka  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200388

Progress of the theory of nonadiabatic electron dynamics beyond the Born-Oppenheimer paradigm in chemical science is presented. We show that a new field of theoretical chemistry, namely, chemistry of nonadiabatic electron dynamics has been initiated and developed by illustrating some of our systematic applications to elementary molecular processes, chemical reactions, diffusive dynamics of densely quasi-degenerate electronic states, and so on.

**Keywords:** Infinite-order two-component | Local unitary transformation | Divide-and-conquer  

**Development of Linear-Scaling Relativistic Quantum Chemistry Covering the Periodic Table**

Hiromi Nakai  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210091

Accurate and efficient two-component relativistic quantum chemistry, which causes a paradigm shift, has been launched. The key ingredients are local unitary transformation (LUT), divide-and-conquer (DC), frozen core potential (FCP), and accompanying coordinate expansion with a transfer recurrence relation (ACE–TRR). This award account explains the outline of the theoretical aspects, followed by numerical demonstrations.
**Keywords:** Concentration fluctuation | Kirkwood-Buff integral | Mesoscopic

**The Solution Chemistry of Mixing States Probed via Fluctuations: a Direct Description of Inhomogeneity in Mixing**

Keiko Nishikawa


Image of disordered distribution of molecules in a binary system. Two types of molecules are randomly mixed in the left figure, while the same type of molecules form clusters in the right figure. Such differences in mixing scheme are quantitatively expressed as “concentration fluctuation”.

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**Keywords:** Water dynamics | Water phase transitions | Supercooled water

**Dynamical Behavior of Water; Fluctuation, Reactions and Phase Transitions**

Iwao Ohmine* and Shinji Saito*


Dynamics of water over a wide range of temperatures and effects of water on reactions and biological functions are theoretically investigated at the molecular levels. In deeply supercooled region, water relaxation process and glass-transition mechanism are explored. On phase-transitions and chemical reactions, water freezing and ice melting processes are analyzed. On biomolecular functions, water roles are examined in ion-channel, photoactive yellow protein and reaction center.
This Account summarizes my recent attempts to manipulate molecular assembly structures and their functions particularly the photochemical properties on inorganic host nanosheet materials constructed via multiple electrostatic interactions, as proteins do in the living systems such as in photosynthetic complexes.
Analytical and Inorganic

Keywords: Applied supramolecular chemistry | Chemical sensing | Supramolecular device
Design of Supramolecular Sensors and Their Applications to Optical Chips and Organic Devices
Tsuyoshi Minami
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200233

More than half a century has passed since the origin of supramolecular chemistry, while its real applications in society are still challenging. To this end, the author has carried out a comprehensive study on supramolecular analytical chemistry from single molecule to device scale. This account summarizes the author’s recent achievements for chemical sensors including the design of artificial receptors, optical chemosensor arrays, and organic field-effect transistors.

Keywords: Single-molecule magnets | Single-chain magnets | MX-Chains
Next Generation Multifunctional Nano-Science of Advanced Metal Complexes with Quantum Effect and Nonlinearity
Masahiro Yamashita
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200257

In this Award Account, I stressed what science is. Do you ever contemplate about what science is? I believe that science is to create new research fields that are original and creative with new concepts. In order to do so, it will take 40 years or more. Therefore, scientists have only one chance in their lifetimes. I have establish my research field titled “Multifunctional Nano-Science of Advanced Metal Complexes with Quantum Effect and Nonlinearity”.

T. Minami
M. Yamashita
Self-assembly mechanism of crystal nuclei of organic crystals and metal–organic frameworks was investigated using single-molecule-level electron microscopic imaging and bulk analysis. Statistical information on the size and structure of the individual prenucleation clusters allowed us to study how the nucleating crystals acquire order and dimensionality in the nucleation process.

Coordination asymmetry strategy is envisioned to architect asymmetrical and/or chiral structures and/or electronic states through formation of metal coordination complexes, leading to functional material systems with certain anisotropy and selectivity. This review article explains expansions of the nanoarchitectonics concept to coordination asymmetry through collecting recent examples in the field of coordination asymmetry.
**Keywords:** Gold cluster | N-Heterocyclic carbene | Luminescence

**Reconstituting C-Centered Hexagold(I) Clusters with N-Heterocyclic Carbene Ligands**

Zhen Lei, Xiao-Li Pei, Hitoshi Ube, and Mitsuhiko Shionoya*


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210060

N-Heterocyclic carbene ligands were successfully utilized to reconstitute C-centered hexagold(I) clusters. Strong intramolecular C(sp³)–H…Au interactions with the minimum gold-hydrogen distance of 2.566 Å were found as a key structural feature in the resulting clusters. Significantly enhanced absorption and shifted luminescence were also observed.

**Keywords:** Oxynitrides | Thin film | Metastable

**Exploring Metastable Oxynitrides by Thin Film Growth Approach**

Yasushi Hirose* and Tetsuya Hasegawa


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20210033

Metal oxynitrides are expected to show unique chemical and physical properties suitable for various applications. However, there is a huge unexplored chemical space due to their thermal instability and high reaction temperature required in conventional bulk synthesis. In this account, we will overview recent studies on thermally nonequilibrium thin film synthesis of oxynitrides, especially focusing on exploration of metastable phases.
Supramolecular thermocells use thermo-responsive host–guest interaction to regenerate electrochemical energy from low-grade heat sources. The selective transport of a redox species carried by the host molecule creates a concentration gradient of the redox species and generates the thermoelectric voltage. Design principles and promising candidates of the host–guest pairs for efficient supramolecular thermocells are presented here.

The chemistry of molecular confinement has been extremely spread as chemists can treat molecular aggregates and larger molecules within large cavities of self-assembled hosts. In this account, we introduce the molecular confinement effects of our self-assembled cages as the phenomena in which new properties of molecules emerge in the chemically defined cavities.
**Keywords:** Polythiophene | Chemical sensor | Supramolecular device

**Polythiophene-Based Chemical Sensors: Toward On-Site Supramolecular Analytical Devices**  
Yui Sasaki, Xiaojun Lyu, Wei Tang, Hao Wu, and Tsuyoshi Minami*  

Polythiophene is a promising material for chemical sensors owing to tunable chemical and physical properties, while on-site sensing in aqueous media using polythiophene-based solid-state devices is still challenging. We herein propose several strategies to realize supramolecular analytical devices in accordance with the philosophy of “lateral thinking with established technology”.

**Keywords:** Charge transfer | Metal–organic framework | Magnetism

**Charge Manipulation in Metal–Organic Frameworks: Toward Designer Functional Molecular Materials**  
Hitoshi Miyasaka  

How do we design functional frameworks that are sensitive to stimuli? We have focused on the design of electron-conjugated charge-transfer (CT) frameworks comprising electron donor (D) and electron acceptor (A) sites or subunits having a $D_mA_n$ formula; we denote these frameworks D/A-MOFs, which allow their charge distribution to be tuned by varying the intralattice CT between the D and A components.
Concentrated battery electrolytes have been outside the focus of research because of their decreased ionic conductivity. However, various unusual properties and functions have been recently discovered, which arise from their unique coordination states. This account introduces our original contributions to the development of concentrated electrolytes and provides future visions on advanced batteries using this new concept of electrolyte.

Keywords: Batteries | Electrolytes | Coordination

Concentrated Battery Electrolytes: Developing New Functions by Manipulating the Coordination States
Yuki Yamada
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20190314

In this review, we address 2-dimensional layered hydroxides with low toxicity, high solubility in body fluid, high tumor targeting efficiency and large drug loading capacity, etc. And we highlight its recent advances for diagnosis and imaging functions, and try to provide outlook on possible future progress and challenges in the view point of nanomedicine.

Keywords: 2-Dimensional nanomaterials | Diagnostics | Medicinal imaging application

2-Dimensional Nanomaterials with Imaging and Diagnostic Functions for Nanomedicine; A Review
Sairan Eom, Goeun Choi, Hiroyuki Nakamura, and Jin-Ho Choy*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20190270
The combination of ultrasound with nanoparticles enables the development of different types of therapeutic strategies. In this work, we aim to provide an overview of the main types of inducible responses that have been reported in the literature in this context, divided in: inducing drug release, producing ultrasound-derived biological effects, modifying nanoparticle biodistribution and developing theranostic agents.

Keywords: Ultrasound | Nanomedicine | Stimuli-responsive
**Ultrasound-Activated Nanomaterials for Therapeutics**
Juan L. Paris* and María Vallet-Regí*

To expedite the preparation of practical molecular probes for life science research, such as imaging probes for positron emission tomography (PET), we have proposed a new concept, “molecular renovation strategy.” In this account is described our recent efforts and related methods to realize this concept, including transition metal-catalyzed borylation reactions via cleavage of stable chemical bonds and deborylative radiolabeling reactions.

Keywords: Molecular probe | Borylation | Radiolabeling reaction
**Molecular Renovation Strategy for Expeditious Synthesis of Molecular Probes**
Takashi Niwa* and Takamitsu Hosoya*
**Keywords:** Amorphous alloys | Metallic glasses | Porous metals

**Recent Applications of Amorphous Alloys to Design Skeletal Catalysts**

David Salinas-Torres, Ai Nozaki, Miriam Navlani-García, Yasutaka Kuwahara, Kohsuke Mori, and Hiromi Yamashita*


Amorphous alloys attract great attention in the field of catalysis because their physical and chemical properties make them suitable materials to be used as catalysts at industrial scale. In this review we report some representative examples of amorphous alloys applied to hydrogenation, dehydrogenation, and oxidation reactions.

**Keywords:** Molecular machine | Nanoarchitectonics | Dynamism

**Dynamism of Supramolecular DNA/RNA Nanoarchitectonics: From Interlocked Structures to Molecular Machines**

Xingguo Liang,* Lin Li, Jiaxuan Tang, Makoto Komiyama,* and Katsuhiko Ariga*


This review describes the dynamic features of supramolecular DNA/RNA nanoarchitectonics leading to molecular machines. Significant roles of DNA/RNA rings, catenanes, rotaxanes, and their connectors are emphasized. Applications of these parts to molecular machines (e.g., shuttles, walkers, pumps, robots, and logic gates) are widely covered.
**Keywords:** Precursor approach | Aromatic compounds | Organic semiconductors

**Synthesis and Morphological Control of Organic Semiconducting Materials Using the Precursor Approach**

Hiroko Yamada,* Daiki Kuzuhara, Mitsuharu Suzuki, Hironobu Hayashi, and Naoki Aratani


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200130

The precursor approach is a useful method to synthesize pure π-extended aromatic compounds that cannot be prepared via traditional organic synthesis in flasks. This account focuses on the precursor approach for the synthesis and morphological control of functional aromatic compounds for organic field effect transistors and organic photovoltaics in our group in the last decade.

**Keywords:** Mesoporous silica | Catalysis | Environmental remediations

**Functional Mesoporous Silica Nanomaterials for Catalysis and Environmental Applications**

Baljeet Singh,* Jongbeom Na,* Muxina Konarova, Toru Wakihara, Yusuke Yamauchi, Carlos Salomon, and Manoj B. Gawande*


https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200136

Mesoporous silica nanomaterials (NMs) have been extensively studied for various applications, due to their high surface area and uniform pore size distribution. This review highlights the recent progress in mesoporous silica NMs, especially nanoparticles (NPs), and their applications for heterogeneous catalysis, use as hard-templates, environmental remediations, and adsorbents for CO₂ capture.
Keywords: Ion channel | Poly(ethylene glycol) | Polymorphism

Biofunctional Molecules Inspired by Protein Mimicry and Manipulation
Takahiro Muraoka
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20190315

This account describes synthetic approaches to develop functional molecules based on the concept to mimic and manipulate proteins. Inspired by the multiblock structures seen in transmembrane proteins, synthetic supramolecular ion channels that respond to ligand and membrane tension are developed. Functionalization of poly(ethylene glycol) by structuring allows for controlling the thermal properties and protein aggregation suppression.

Keywords: PI polyamides | Sequence-specific DNA binding | Regulation of gene expression

Sequence-Specific PI Polyamides Make It Possible to Regulate DNA Structure and Function
Toshikazu Bando and Hiroshi Sugiyama*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20190311

Based on the property of DNA sequence-specific binding, various types of PI polyamides conjugates were mainly developed to regulate the specific gene expression. In future, versatile bioinformatics for understanding gene function and structure would be provided by PI polyamides conjugates. (This graphic of DNA-PI polyamide complex was based in PDB: 3OMJ.)
**Keywords:** Living radical polymerization | Tellurium | Photochemistry

**Photoactivation of Organotellurium Compounds in Precision Polymer Synthesis: Controlled Radical Polymerization and Radical Coupling Reactions**

Shigeru Yamago  


Organotellurium-mediated radical polymerization (TERP) under photoirradiation, compared to TERP under thermal conditions, significantly increases the synthetic advantages and provided highly structurally controlled polymers. Switching from TERP to a radical coupling reaction by changing the light intensity is also possible. These synthetic methods provide new opportunities in macromolecular engineering for fabricating functional polymer materials with improved and/or new functions.

**Keywords:** Phosphine-free | Heck reaction | Suzuki coupling

**Advances in C-C Coupling Reactions Catalyzed by Homogeneous Phosphine Free Palladium Catalysts**

Lakshmi Kantam Mannepalli,* Chandrakanth Gadipelly, Gunjan Deshmukh, Pravin Likhar, and Srinivas Pottabathula  


Development of phosphine-free palladium catalysts using N-donor ligands for the Heck and Suzuki reactions provides an efficient route for C-C coupling reaction. The design of palladium catalysts using an anionic carboxyamide and anionic urea as an ancillary ligands provides a new opportunity for the development of transition metal catalysis under phosphine-free conditions with an achievement of high Turnover numbers for C-C coupling activity with various deactivated aryl systems.
We have developed two novel approaches for the construction of artificial metalloenzymes. The first example is the use of apo-ferritin for hydrogenation of olefins and Suzuki-Miyaura C-C coupling by employing Pd$^0$ nano-clusters and Pd$^{2+}$(η$^3$-C$_3$H$_5$) complexes, respectively. The second approach is the use of “decoy molecules” to change substrate specificity of P450s, allowing epoxidation and hydroxylation activities toward nonnative organic substrates.

**Keywords:** Ferritin | Cytochrome P450 | Metalloenzyme Molecular Design and Regulation of Metalloenzyme Activities through Two Novel Approaches: Ferritin and P450s  
Yoshihito Watanabe,* Yuichiro Aiba, Shinya Ariyasu, and Satoshi Abe  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20190305

In this account, we summarize our recent achievements in our exploration of functional PAHs and GNRs with novel structures and properties, including dibenzo[hi,st]ovalenes, which demonstrated strong red luminescence and stimulated emission, and double [7]carbohelicenes with intriguing structural and optical properties. We also accomplished GNRs with unprecedented zigzag edge structures, leading to an emergence of topological electronic states.

**Keywords:** Polycyclic aromatic hydrocarbon | Nanographene | Graphene nanoribbon  
Syntheses and Characterizations of Functional Polycyclic Aromatic Hydrocarbons and Graphene Nanoribbons  
Xiushang Xu, Klaus Müllen,* and Akimitsu Narita*  
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20190368
This comprehensive and critical review present advantages and limitations of existing molecular probes for detecting alloforms of core biomarkers (Aβ and tau). Advocate the importance of detecting core and indirect biomarkers in the brain and bio-fluids through multiplexed and multimodal approaches to generate fingerprints that accurately distinguish between healthy and disease condition to facilitate early AD diagnosis.

**Keywords:** Alzheimer’s disease | Core and indirect biomarkers | Multiplexing and multimodal diagnosis

**Molecular Tools to Detect Alloforms of Aβ and Tau: Implications for Multiplexing and Multimodal Diagnosis of Alzheimer’s Disease**

Harshit Arora, Madhu Ramesh, Kolla Rajasekhar, and Thimmaiah Govindaraju*


The development and refinement of peptide synthesis has entered a phase of rapid advance. Although the racemization-free formation of peptide bonds has been pursued for more than a century, this long-standing challenge continues to attract considerable interest from many scientists. We have developed over the last five years six novel methodologies for peptide bond-forming reactions to address these issues.

**Keywords:** Lewis acids | Substrate control | Peptides

**Game Change from Reagent- to Substrate-Controlled Peptide Synthesis**

Wataru Muramatsu,* Tomohiro Hattori, and Hisashi Yamamoto*


Light-induced difference FTIR spectroscopy is a powerful, sensitive and informative method to study structural dynamics of photoreceptive proteins. Strong absorption of water in the IR region is always an issue in this method. However, if water content in the sample is controlled during measurements, this method can provide detailed structural information on a single protein-bound water molecule in animal and microbial rhodopsins.

Photodynamic therapy is a clinically accepted treatment for cancer therapies in several countries around the world. Photosensitizers (PS) have enhanced the photophysical and photochemical properties of PDT. Yet, they have some side effects. However, glycosylation of PS could increase the plasmatic life time, solubility as well as specific targeting of cancer cells.
The progress on the chemistry of heteroaromatic compounds developed in our group is summarized. The topic involves C–H functionalization of azoles and thiophenes with organic electrophiles, cross coupling polymerization leading to conjugated polymers showing functionalities as materials, and design of a novel class of heterobiaryls showing molecular asymmetry, where we define as winding vine-shaped molecular asymmetry.

The goal of this account is to detail the steps taken by our group for the development of glycosylated artificial metalloenzymes (GArMs), which we are interested in developing as biotechnological tools for potential diagnostic and therapeutic applications.
Keywords: Carboxamides | Amines | Reduction

Reductive Functionalization of Carboxamides: A Recent Update
Derek Yiren Ong, Jia-hua Chen, and Shunsuke Chiba*
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200182

This review highlights and discusses recent advances on deoxygenative reductive functionalization of carboxamides for the synthesis of α-branched amines, that are initiated by controlled hydride reduction of carboxamides using aluminum hydrides, the Schwartz's reagent, transition-metal catalyzed/mediated hydrosilylation or sodium hydride-iodide composite.

Keywords: Structure determination | Chemical synthesis | Natural products

Structure Determination, Chemical Synthesis, and Evaluation of Biological Activity of Super Carbon Chain Natural Products
Tohru Oishi
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200151

Marine microorganisms are known to produce natural products, so called super carbon chain compounds whose molecular weights exceed one thousand. In this article, our recent achievements are reviewed on structure determination, chemical synthesis, and evaluation of biological activity of super carbon chain natural products focusing on amphidinol 3 and maitotoxin.
Molecules irradiated with intense laser pulses (field intensity \( \sim 10^{15} \) W/cm\(^2\)) exhibit a variety of characteristic processes, such as tunneling ionization, electron rescattering, high-order harmonics generation and Coulomb explosion, that cannot be seen in a weak light field. These features have attracted attention in the last decades as they provide unique approaches to visualize and manipulate ultrafast dynamics of atoms and molecules. Here we discuss molecular processes in intense laser fields, with focuses on the applications to ultrafast imaging and control of reaction dynamics.
The carbon-based nanomaterials (CNMs), including graphene, carbon nanotubes, and fullerenes, have been applied for the effective separations and sensitive detections in recent years. The fundamental preparation protocols of new separation media consisted of CNMs and a great number of their applications are summarized.

The present article described the design of various peptide nucleic acid (PNA)-based fluorescent probes carrying cyanine dyes for targeting the overhang structures of siRNAs or dsRNA sequences. By virtue of the unique binding selectivity and the significant light-up ability for target dsRNAs, our probes could find new analytical applications that are the analysis of carrier-mediated siRNA delivery process and sequence-selective dsRNA detection.

The carbon-based nanomaterials (CNMs), including graphene, carbon nanotubes, and fullerenes, have been applied for the effective separations and sensitive detections in recent years. The fundamental preparation protocols of new separation media consisted of CNMs and a great number of their applications are summarized.
Microcystin-LR is one of the most toxic and harmful of fresh water toxins causing many accidents and threats to human health. This review summarized recent progress, prevailing detection techniques and future trends of biosensor development.

**Keywords:** Microcystin-LR | Biosensors | Cyanobacteria

**Recent Advancement of Biosensor Technology for the Detection of Microcystin-LR**

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Redox active $\alpha$-diimine ligands were introduced into early transition metals by two synthetic methods: (1) a salt-metathesis reaction by treating ligand-supported metal precursors with the alkali metal salts of $\alpha$-diimines and (2) a salt-free reaction by applying organosilicon compounds to homoleptic metal chlorides in the presence of $\alpha$-diimines. Catalytic performance was developed by taking an advantage of tunable flexibility among neutral, monoanionic, and dianionic coordination modes.

**Keywords:** Early transition metal complex | Redox active $\alpha$-diimine ligand | Salt-free reduction

**Redox-Active $\alpha$-Diimine Complexes of Early Transition Metals: From Bonding to Catalysis**

Kazushi Mashima


MAIRS: Innovation of Molecular Orientation Analysis in a Thin Film
Takeshi Hasegawa* and Nobutaka Shioya
https://www.journal.csj.jp/doi/abs/10.1246/bcsj.20200139

MAIRS is a rapidly being spread as a powerful tool for analyzing the molecular structure in a functionalized thin film in terms of molecular orientation, conformation and polymorph in a quantitative manner. Since MAIRS analysis is uniquely robust to the surface roughness of the film, all kinds of thin films prepared by the spin-coating and drop-casting can be analyzed with a high reproducibility.

Real-Space Studies of Plasmon-Induced Dissociation Reactions with an STM
Emiko Kazuma
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A scanning tunneling microscope (STM) has been applied to the investigation of dissociation reactions induced by the plasmon excited at a nanogap between the STM tip and a metal substrate under light irradiation. The STM analyses combined with density functional theory calculations provided mechanistic insights into the plasmon-induced dissociation reactions at a single-molecule level.
Proton-coupled electron transfers (PCET) in metal complexes are described, mainly focusing on the formation and reactivity of RuIV-oxo, RuIII-oxyl, and RuIII-pterin complexes. Water oxidation by a CoIII complex and CO₂ reduction by NiII complexes are also discussed in light of PCET.