

Recent Topics in Advanced Materials Science

Recent Topics in Advanced Materials Science:

Element by Element

By

Akio Makishima

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- Fig. 12-1. Synthesis of the tetrablock copolymer. 1: The isoselective pyridylamidohafnium catalyst. ⁱPr: isopropyl. 2, 4: Propylene. 3, 5: Ethylene. 6: Tetrablock copolymer.
- Fig. 12-2. The images of the pincer ligands. M is a metal, and A and B are a central donor (A in b) and a link to a lateral donor (B in c), respectively.
- Fig. 12-3. [CCC]X₃-donor pincer ligands for tantalum. (a) [κ^3 -Ar^{Tol2}]-Ta(PMe₃)₂Me₂. (b) [κ^3 -Ar^{Tol2}]-Ta(PMe₃)₂(η^6 -C₆H₆).
- Fig. 13-1. The Mo (or W) catalyst.
- Fig. 13-2. Synthesis of cis, syndiotactic A-alt-B copolymers by a Mo (or W) catalyst, [M]
- Fig. 13-3. Converting benzene ring to cyclohexenes by the complex TpW(NO)(PMe₃)(η^2 -PhCF₃) (a). This figure is published in “Biochemistry for Materials Sciences” by Akio Makishima 2018, page 251, copyright: Elsevier.
- Fig. 13-4. One-pot synthesis using the Ag₄₈Pd₅₂/WO_{2.72} catalyst. (a) One-pot aromatization of 2-nitrophenol and aldehyde to benzoxazole. (b) One-pot

- hydrogenation of ArR-NO₂ to ArR-NH₂. (c) One-pot aromatization of 2-nitroacetophenone and aldehyde to quinazolines.
- Fig. 13-5. a-Molybdenum diboride (a-MoB₂).
- Fig. 13-6. Ultrathin layers of transition-metal dichalcogenides (2D-TMD) device for photodetection. The input light is enhanced by the e-h pair generation effect by 350 %. The thickness of each element is at the single-atomic level. The small voltage is supplied by electrodes.
- Fig. 13-7. Cross-sectional view of "Atomristors".
- Fig. 13-8. (a) The $\epsilon^{94}\text{Mo}$ vs. $\epsilon^{95}\text{Mo}$ plot. (b) The $\epsilon^{183}\text{W}$ vs. $\epsilon^{182}\text{W}$ plot. NC and CC indicate the "non-carbonaceous" iron meteorite group and the "carbonaceous chondrite" iron meteorite group, respectively.
- Fig. 14-1. A schematic diagram of a molecular assembly for overall water splitting reaction. PS, WOC, and HEC indicate a photosensitizer, a water oxidation catalyst, and a hydrogen evolving catalyst. (The figure is modified from Kärkäs et al., 2014)
- Fig. 14-2. A schematic diagram of photosystem II, in which a Mn₄CaO₅-cluster oxidizes water into O₂+4H⁺+4e⁻.
- Fig. 14-3. The typical ruthenium (II) polypyridyl-type complex, [Ru(bpy)₃]²⁺ where bpy means 2,2'-bipyridine.
- Fig. 14-4. The blue dimer.
- Fig. 14-5. The Ru WOC, *in, in*-[[Ru(tpy)(H₂O)]₂(μ -bpp)]³⁺.
- Fig. 14-6. [Ru(bda)bpb]₃. bda = 2,2'-bipyridine-6,6'-dicarboxylic acid; bpb = 1,4-bis(pyrid-3-yl) benzene.
- Fig. 14-7. Lewis acid catalyzed enantioselective cycloaddition of 2'-hydroxychalcone. (OTf: trifluoromethanesulfonate or CF₃SO₃; t-BuPyBox: see Fig. 14-8; *i*-Pr: isopropyl; OAc: acetate; CFL: compact fluorescent lamp; rt: room temperature).
- Fig. 14-8. The chiral stereodifferentiating ligand, t-BuPyBox. t-Bu is tert-butyl.
- Fig. 14-9. The p _{π} -d _{π} -p _{π} π -conjugation.
- Fig. 14-10. The anti-aromatic five membered rings of osmium.
- Fig. 14-11. CCCC-pentadentate chelates of osmium.
- Fig. 14-12. (a) A new ruthenium catalyst. (b) The selectivity of the catalyst.
- Fig. 14-13. (a) An experimental set up. Ru catalysts are attached to a glass slide via a polymer chain and a magnetic particle, and pulled up by a pair of magnetic tweezers. (b) The reaction follows the Wait and Jump steps.
- Fig. 14-14. (a) The Ru catalyst **1** and the norbornene probe **2**, which only flashes when ring-opening metathesis polymerization (ROMP) occurs in the stationary condition. Mes= 2,4,6-trimethylphenyl. Cy= cyclohexane (-C₆H₁₁). (b) A spatiotemporal resolution experiment which reveals reaction dynamics through molecular catalysts within polymers. Option A: Catalysis occurs in the solution, which means no areas glow. Option B: Catalysis occurs after precipitation, thus glowing lights are observed.
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- Fig. 15-1. Rh catalyst for C-C and C-H bonds activations. (a) Total reaction. (b) Details of the reaction (the reactions are simplified). (A) The shaded circles

- indicate the positions. **(B)** Rh cuts the five member ring. **(C)** C-C activation, and Rh forms the six member ring. **(D)** C-H activation, and Rh forms another six member ring. **(E)** Rh is removed with forming a new six member ring and a methyl.
- Fig. 15-2. New Rh catalyst.
- Fig. 15-3. Synthesis of 1-phenylalkenes via oxidative arene vinylation.
- Fig. 15-4. (a) Schematic diagram of site-specific modification of an antibody by dirhodium metalloprotein catalyst (1) using alkyne-functionalized diazo (2). 1. Structure of dirhodium complex attached to carboxylate group of glutamic acid residue on the peptide. (b) The dirhodium core acts as a reactive catalytic center through metalcarbene formation and a coordination site for Lewis basic side chain in a protein. (c) Schematic diagram of azide-alkyne cycloaddition reaction (click chemistry) between alkyne-functionalized antibodies and azide-fluorophore (shown as a ball). Fluorophore can be added to cancer drugs.
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- Fig. 15-6. (a) Dirhodium catalysts for the non-activated secondary and tertiary C-H bonds. (b) An example of the reaction of the tertiary C-H bonds to the dirhodium catalyst.
- Fig. 16-1. Chiroptical sensing by Pd(II) complex. Ph = phenyl, R = various groups. TBAOH is tetrabutylammonium hydroxide, $(\text{C}_4\text{H}_9)_4\text{NOH}$.
- Fig. 16-2. Tested amino acids by De los Santos and Wolf (2016).
- Fig. 16-3. Examples of important molecules with β -lactams. (a) Penicillin (antibiotic); (b) Zetia (cardiovascular drug); (c) Chartelline C (natural product).
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- Fig. 16-5. Enantioselective intermolecular coupling phenols and allylic alcohols.
- Fig. 16-6. The intermolecular oxa-Heck reaction by the Pd catalyst.
- Fig. 16-7. Heck reactions. (a) The Heck reaction. (b) Mizoroki et al. (1971). (c) Heck et al. (1972).
- Fig. 16-8. Dimetalated pincer complexes. (a) SCS pincer of Loeb and Shimizu; (b) van Koten's NCN pincer; (c) NCN pincer used by Shinoya in a molecular "ball bearing"; (d) Dipalladium (II) complex of Lohrman et al. (2016).
- Fig. 16-9. Pt complex with Lewis acidic Sb-ligand. (a) $(\text{o}-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_2\text{SbCl}_2\text{-PtCl}$ (1). (b) $(\text{o}-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4)_2\text{SbOTf}_2\text{PtCl}$ (2). When a nucleophilic substrate such as an alkyne reacts with (b), platinum reactive site is unmasked (see arrows) leaving (c) without a chloride removing reagent.
- Fig. 16-10. Reactions catalyzed by the Pt complex, 2 (Fig. 16-9b).
- Fig. 16-11. Schematic diagram of the catalytic bifunctional template.
- Fig. 16-12. A template material, a yield, and site selectivity. Ac-Gly-OH and HFIP are N-acetyl-protected glycine ligand and hexafluoroisopropanol. (a) A reaction targeting phenylpyridine. (b) A reaction targeting quinolone.
- Fig. 16-13. (a) Preparation of $(\text{CH}_3)_2\text{CHCONHAr}_F$ from isobutyryl chloride. Isobutyryl chloride is easily formed from the reaction of isobutyric acid with SOCl_2 . (b) Enantioselective C-H arylation of isobutyric acid. (c) Enantioselective C-H alkenylation and alkynylation of isobutyric acid.

- Ar(Het)= (hetero)aryl group; Ar_F=4-(CF₃)C₆F₄; Me= Methyl; TFA= trifluoroacetate; TIPS= triisopropylsilyl group.
- Fig. 16-14. (a) C-S metathesis reaction by palladium catalyst. (b) Depolymerization of thermoplastic polymer. (c) Late-stage derivatization (i.e. direct modification of the final product) of an antipsychotic drug.
- Fig. 16-15. Platinum-containing cancer drugs. (a) Cisplatin. (b) Oxaliplatin. (c) Carboplatin. This figure was published in “Biochemistry for Materials Sciences” by Akio Makishima 2018, page 181, copyright: Elsevier.
- Fig. 16-16. (a) Starting materials. (b) The product identified in 1964. (c) The corrected composition of the product in 2017. (Ph = phenyl).
- Fig. 16-17. (a) Secondary electron microscope (SEM) image of the PdAu nanoparticle. (b) Up. Two dimensional histogram of product positions on the nanoparticle in (a) in $50 \times 50 \text{ nm}^2$ bins. The nanoparticle has been reoriented to align horizontally. Outer white line, white circle, and the contour of the Au particle are determined from the SEM image in (a). (b) Down. Segmentation of a typical PdAu nanoparticle: regions of monometallic Pd (Pd), Au-doped Pd next to the Pd–Au interface (PdAu), monometallic Au (Au), and Pd-doped Au next to the Pd–Au interface (AuPd). Image credit: Chen, G., Zou, N., Chen, B., Sambur, J. B., Choudhary, E., et al. 2017. Bimetallic Effect of Single Nanocatalysts Visualized by Super-Resolution Catalysis Imaging. *ACS Central Science*, 3, 1189–1197. (c) Proposed chemical equation of photodriven disproportionation reaction of resazurin (Rz) to resorufin (Rf) and a one-electron-oxidized radical species (Rz[•]) catalyzed by Pd or Au catalysts.
- Fig. 16-18. Conversion of Pd and Au into water-soluble complexes by mild conditions. (a) Traditional methods. (b) New methods.
- Fig. 16-19. (a) The tested Suzuki-Miyaura cross-coupling reaction. (b) Heat output (kJ) according to time by Yang et al. (2018). (c) Chemical formulas of Pd(dppf)Cl₂, DMSO, DMF, and dioxane.
- Fig. 16-20 Pd catalyst for C-H fluorination.
- Fig. 17-1. The schematic diagram of the stable crystal with α -cyclodextrin [AuBr₄]⁻ and K⁺.
- Fig. 17-2. Schematic diagram for direct gold-nanoparticle integration by laser ablation.
- Fig. 17-3. All-metal aromatic sandwich Au-Sb cluster [Sb₃Au₃Sb₃]³⁻.
- Fig. 17-4. New synthesis of the rheumatoid arthritis drug leflunomide (Arava), which shows a new trifluoromethylation reaction.
- Fig. 17-5. Phosphine-calixarene gold chloride complexes used as precursors for the synthesis of Au clusters (a) a1, a2, and (b).
- Fig. 17-6. Nanoparticle surfactants make a monolayer skin on a droplet: X= Fe₃O₄ or PbS.
- Fig. 18-1. The structure of [La(η^4 -Sb₄)₃]³⁻. La can be replaced with Y, Ho, Er, or Lu.
- Fig. 18-2. Formation of Chromogen I to GlcNAc.
- Fig. 18-3. (a) The arrangement of nine Ln³⁺ ions of [Ln₉(μ_4 -O)(μ_3 -OH)₈(LH)₄(OAc)₄(H₂O)₁₂] 5ClO₄·24H₂O (Ln = Gd or Dy). (b) The coordination of LH²⁻, where L is Chromogen I.

- Fig. 18-4. Single-molecule magnet (SMM); $[\text{Dy}(\text{Cp}^{\text{III}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ with $\text{Cp}^{\text{III}} = \{\text{C}_5\text{H}_2\text{Bu}_3-1,2,4\}$ and $\text{Bu} = \text{C}(\text{CH}_3)_3$.
- Fig. 18-5. Molecular structure of Ce *bis*(carbene) complex ($[\text{M}(\text{BIPM}^{\text{TMS}})_2]$; $\text{M} = \text{Ce}, \text{U}, \text{Th}$; $\text{BIPM}^{\text{TMS}} = \{\text{C}(\text{Ph}_2\text{PNSiMe}_3)_2\}^{2-}$) at 150K. The structures of U and Th complexes are very similar. Hydrogen atoms and lattice solvent are not shown for clarity.
- Fig. 18-6. Crystal structure of a berkelium coordination compound. The central Bk(III) ion is coordinated by three monoprotonated dipicolinate ligands in tridentate O,N,O fashion.
- Fig. 18-7. Thorium and uranium complexes.
- Fig. 18-8. (a) 6-Carboxyfluorescein–glucose. (b) Dysprosium–1,4,7,10-tetraazacyclododecane–1,4,7,10-tetraacetic acid–glucose (Glc-DOTA-Dy(III)).
- Fig. 18-9. Mechanism of the Pt-CeO₂ catalyst. A. An oxygen vacancy exists in the catalyst. B. The oxygen vacancy moves to the surface of the catalyst. C. When a water molecule comes, it is absorbed in the vacancy, and Pt-Ce-OH groups are formed. These sites become active sites for CO oxidation.
- Fig. 18-10. Cerium containing methanol dehydrogenase from *Methylacidiphilum fumariolicum* SolV by Pol et al. (2014). Image Credit: NGL Viewer (A.S. Rose et al. (2018) NGL viewer: web-based molecular graphics for large complexes. Bioinformatics doi:10.1093/bioinformatics/bty419), and RCSB PDB 4MAE.
- Fig. 19-1. Potassium tert-butoxide/ hydrosilane (KOSi) homogeneous hydrodesulfurization.
- Fig. 19-2. (a) Ru catalyst, Ru-11. (b) Pd catalyst, IC-1. (c) Ru catalyst, Ru-CAAC. (d) The target reaction (isomerization ethenolysis of RME).
- Fig. 20-1. Markovnikov's rule. (a) Hydration. (b) Oxidation. The reactant in the parentheses shows one against Markovnikov's rule.
- Fig. 20-2. The anti-Markovnikov hydrations of alkenes. (a) Indirect synthesis of alcohols from olefins with anti-Markovnikov selectivity. (b) Grubbs' triple relay catalysis system. Shvo's catalyst = see (c); BQ = benzoquinone; Bu = butyl; Ph = phenyl; Pr = propyl. (c) The Shvo's catalyst (Shvo and Czarkie, 1986). Ph = phenyl. (d) The new anti-Markovnikov hydration of alkenes via the radical cation by Hu et al. (2017). (e) The ACR⁺-Mes⁻ catalyst. Ph = phenyl.
- Fig. 20-3. Proposed mechanism of a new anti-Markovnikov hydration by Hu et al. (2017).
- Fig. 20-4. (a) The anti-Markovnikov law reaction with a new enzyme, aMOx. (b) The structure of P450 monooxygenase PikC (PDB: 2WHW) without the heme from Li et al. (2009) is shown. This is the base structure of aMOx. Image credit: NGL Viewer (A.S. Rose et al. (2018) NGL viewer: web-based molecular graphics for large complexes. Bioinformatics doi:10.1093/bioinformatics/bty419), and PDB 2WHW.
- Fig. 21-1. Cu-zeolites catalyst. In the model by Paolucci et al. (2017), Cu ions with NH₃ travels to form oxygen-bridged dimer complexes. (Figure is based on Jacoby (2017).)

Fig. 21-2. (a) An electron-donating molecule, N,N,N',N'-tetramethylbenzidine (TMB). (b) An electron-accepting molecule, 2,8-

bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT).

Fig. 22-1. Crystal structures of (a) α - (DMEN)PbBr₄ (DMEN = 2-

(dimethylamino)ethylamine); (b) (DMAPA)PbBr₄ (DMAPA = 3-(dimethylamino)-1-propylamine); (c) (DMABA)PbBr₄ (DMABA = 4-dimethylaminobutylamine).

Fig. 22-2. 1931 color space chromaticity diagram. Image credit: Wikipedia.

https://upload.wikimedia.org/wikipedia/commons/3/3b/CIE1931xy_blank.svg.

Fig. 22-3. (a) Optical images under ambient light and 365 nm UV lamp. (b) Steady-state PL emission spectra of MAPbX₃ NCs@Pb-MOF. (1: MAPbCl₃, 2: MAPbCl₂Br, 3: MAPbClBr₂, 4: MAPbBr₃, 5: MAPbBr₂I, 6: MAPbBrI₂, 7: MAPbI₃). Image Credit: Zhang, C., Wang, B., Li, W., Huang, S., Kong, L. et al. 2017. Conversion of invisible metal-organic frameworks to luminescent perovskite nanocrystals for confidential information encryption and decryption. *Nature Communications*, 8: 1138. DOI: 10.1038/s41467-017-01248-2.

Fig. 23-1. Cuboctahedron building unit. (a) Cuboctahedron is made of six square faces and eight triangle faces. One center and three corners of one triangle face are composed of the uranium node (UO₂(RCOO)₃) and three organic linkers, respectively. (b) Two cuboctahedron cages are connected by a single triangular face.

Fig. 23-2. (a), (c), (e), and (g). From secondary pentagonal to tertiary icosidodecahedron structures. (b), (d), (f), and (h). From secondary hexagonal to tertiary rectified hexakaidecahedron structures.

Fig. 23-3. (a) and (c). The quaternary tetrahedron structure is formed from the tertiary icosidodecahedron structure (the left ball indicates the structure of Fig. 23-2g). The connecting bond corresponds to the pentagon prism in Figs. 23-2a, c, and e. (b) The quaternary tetrahedron structure is formed from the tertiary rectified hexakaidecahedron structure (the right ball indicates the structure of Fig. 23-2h). The connecting bond that corresponds to the hexagon prism appears in Figs. 23-2b, d, and f. (d) The quaternary diamond-topology structure is formed from the tetrahedron structure of (b). (e) The final structure of NU-1301 is formed by putting the tetrahedron of (b) into the space of the diamond structure (d).

Fig. 23-4. Schematic diagram of monolithic and powder MOF synthesis. (a) A metal and organic ligand solution were mixed. (b) HKUST-1 primary particles were made. (c) Wet gel is formed. (d) Powder was made at a high temperature or under a vacuum. (e) Dense monolithic MOF, _{mono}HKUST-1 was made under mild drying conditions.

Fig. 23-5. (a) Structure of BODCA-MOF. (b) ¹H NMR spectra of crystalline BODCA-*d*-MOF.

Fig. 24-1. Schematic diagram of a water harvesting system.

Fig. 24-2. (a) H₂BTDD (bis(1H-1,2,3-triazolo [4',5'-i])dibenxo[1,4]dioxin). (b) Structure of Co₂Cl₂(BTDD) (I) projected along the *c* axis. Hydrogen atoms are omitted for clarity. At low relative humidity (RH), water is absorbed at the

- open coordination sites of the Co atoms, decreasing the pore diameter from above to below. Image credit: Rieth et al. (2017), American Chemical Society.
- Fig. 24-3. Comparison of MOF and zeolites investigated for water sorption. Materials that take up water between 10% and 30% RH are desirable for their strong affinity for water and their relative ease of regeneration. The rightmost "1" shows the work of Rieth et al. (2017). RH indicates the relative humidity. Image credit: Rieth et al. (2017), American Chemical Society.
- Fig. 24-4. Water purification column using polyoxometalate supported liquid phases (POM-SILPs) based on lipophilic POM-ILs supported on porous silica.
- Fig. 24-5. Aquaporin-1. 1J4N by Sui et al. (2001) from PDB. (a) The top view. The protein is embedded through the membrane in this direction. The water molecule passes the membrane through the channel in the center. (b) The side view. The pass of water is covered with hydrophobic α -helix structures. Image credit: NGL Viewer (A.S. Rose et al. (2018) NGL viewer: web-based molecular graphics for large complexes. Bioinformatics doi:10.1093/bioinformatics/bty419), and PDB 1J4N.
- Fig. 24-6. (a) Perfluorooctanoic acid (PFOA) and (b) β -cyclodextrin (β -CD).
- Fig. 24-7. DFB-CDP (decafluorobiphenyl-cyclodextrin) polymers.
- Fig. 24-8. Possible modes of binding **1** (Meisenheimer complex) with different metal ions and the fluoride anion.
- Fig. 24-9. (a) Tree and seed pods of *Moringa oleifera*. Image credit: https://commons.wikimedia.org/wiki/User:Harveychl#media/File:The_tree_and_seedpods_of_Moringa_oleifera.JPG. (b) *Moringa* seeds. Image credit: https://commons.wikimedia.org/wiki/File:The_seeds_of_Moringa_oleifera.JPG. The photographs A and B were taken by Prof. Chen Hualin.
- Fig. 24-10. *Moringa* seed extract-functionalized sand (*f*-sand) filter. Cationic and antimicrobial proteins in *Moringa* seeds can be dissolved easily and adsorbed onto a sand surface, changing the charge of the sand particles to positive. As pathogens and dirt have a negative charge, this filter removes them.
- Fig. 25-1. The reaction between meta-xylylenediamine (MXDA) and CO₂, which form anhydrous white precipitates (MXDA·CO₂).
- Fig. 25-2. The Grignard reaction.
- Fig. 25-3. (a) Highly stretchable polymer semiconductor film. (b) Chemical compositions of the semiconducting polymer DPPT-TT and the soft-elastmer (SEBS).
- Fig. 25-4. Gas permeable polymers. (a) PTMSP. (b) PIM-1. (c) PIM-TMN-Trip.
- Fig. 25-5. (a) Schematic representation of the selected tripeptide sequences. Each "D F Y" indicates one of the amino acid shown in (b). (b) When X is D, F, or Y in NH₂-CHX-COOH, the amino acid becomes aspartic acid, phenylalanine, or tyrosine, respectively. There are six types of sequences, DFY, DYF, YFD, FYD, FDY, and YDF. Tyrosine is oxidized to phenol, DOPA, and dopaquinone (arrows from left to right) by tyrosinase.
- Fig. 25-6. Self-healing gels. (a) The figure shows the enlarged shape of the gels from the frustrated Lewis pairs (FLPs). Gray lines indicate borane (B) and phosphine (P) functionalized polystyrenes. The short black line connecting B and P shows a diethyl azodicarboxylate molecule, which promotes rapid

- network formation. (b) The chemical formula in the box is the enlarged Lewis acid (P) and base (B) interaction.
- Fig. 25-7. Two polymerizable azo-derivatives: (I) a hydrogen-bonded azopyridine, and (II) a hydroxyl group in the ortho position. Each azo-derivative (7 mol%) was copolymerized with a mixture of a liquid-crystal monoacrylate (RM23, 42 mol%) and a liquid-crystal diacrylate (RM82, 50 mol%), initiated by 1 mol% of the photoinitiator, Irgacure 819 (not shown).
- Fig. 25-8. Mechanism of wave propagation. Schematic diagram of the experimental set-up, showing a polymeric film, under an incidence light source. The small black objects in the film show the azobenzene molecules, which isomerize to cis under the light, resulting in shrinking of the film and causing the force (the small arrows). The shaded parts of the ribbon isomerize back to trans and expand causing the force shown by the round arrows.
- Fig. 25-9. Whisky sensor. (a) The three most discriminating sensor array elements (PAE tongues). (b) GFP fluorescent protein tongues (GFPs tongues). GFP-K36 and GFP-E36 are positively and negatively charged, respectively.
- Fig. 25-10. (a) 1-(-)-Menthol. (b) Nutmeg neolignan (stereomixture). (c) An 8-O-4'-neolignan derivative.
- Fig. 25-11. (a) Dipeptide probe. (b) D-Lactate analog.
- Fig. 25-12. Photosensitive hydrogel.
- Fig. 25-13. Schematic representation of the single molecule detection device structure.
- Fig. 25-14. Schematic illustration of “freeze-spinning” technique, combining “directional freezing” with “solution spinning”. This realizes the continuous and large-scale fabrication of biomimetic fibers with aligned porous structures, mimicking polar bear hair. The silk fibroin solution extruded from a pump controlled syringe is gradually frozen when it passes through a cold copper ring. The frozen fiber is freeze-dried to keep its porous structure. Finally it is woven into a textile. The fiber diameter is $\sim 200 \mu\text{m}$.
- Fig. 26-1. Knot topology. The grey color indicates the basic building block of each knot. The number in (a)–(c) shows the Alexander-Briggs notation. The main number indicates the number of crossings, and the subscript differentiates the knot from others with the same number of crossings (see text). (a) 3_1 (trefoil). (b) 5_1 (pentafoil). (c) 8_{19} . (d) Solomon link. (e) Linear double helicates. (f) Star of David.
- Fig. 26-2. The synthesis method of the molecular with 8_{19} knot.
- Fig. 26-3. Evolution of “sulflower” molecules. (a) Persulfurated benzene (C_6S_6). (b) Fully-substituted circulene (C_{16}S_8). (c) Persulfurated coronene ($\text{C}_{24}\text{S}_{12}$).
- Fig. 26-4. Various carbon nanotubes (CNTs) and carbon nanobelts. (a) Carbon nanotubes (CNTs). (b) Carbon nanobelts. (c) Carbon nanobelt (fused arene system). (d) Carbon nanoring (linked arene system).
- Fig. 26-5. Synthesis route of the Itami belt.
- Fig. 26-6. The synthesis of the pentanuclear complex, $[\text{Pd}_5(\mathbf{L1})_5(\mathbf{L2})_5](\text{BF}_4)_{10}$, where $\mathbf{1}$ is the molecular star. $\text{DMSO} = (\text{CH}_3)_2\text{SO}$.
- Fig. 26-5. A double helical SnIP. (a) Crystal structure projected from a-axis. The $[\text{SnI}]$ and $[\text{P}]$ helices form a double helical SnIP strand. The box shows the unit

- shell. The M and P helices are left- and right-handed. (b) Schematic diagram of the double helix arrangement. The [SnI] and [P] helices rotate along the hypothetical axis, which is shown as the white rod. The captions are the same with (a).
- Fig. 26-7. (a) DNA-based components from the top to the center; the top, triangular brick with three identical recessed docking sites; the next white, V-shaped brick with a different protruding plug pattern on each outward-pointing face; grey, V-shaped white brick; the center, connector brick with docking sites on each of the wide face. (b) The component of (a) was self-assembled to form 1.2 GDa dodecahedron with a diameter of 450 nm.
- Fig. 27-1. (a) Molecular structures of a rotaxane-based molecular machine. Final forms as amino acids are phenylalanine, leucine, and alanine for $n = 1, 2, \text{ and } 3$, respectively. (b) Schematic diagram of rotaxane's ring and thread, and the sequential synthesis of amino acids. As the first ring goes out, the next amino acid (gray balls) is added.
- Fig. 27-2. Schematic diagram of iterative coupling of building blocks indicated by different colors.
- Fig. 27-3. (a) A molecular structure of a molecular machine with the arm at the left side. (b) The same machine with the arm at the right side. Only the joint part is shown. (c) An example of a product (S)-(S). (d) A schematic figure of the molecular machine. When the arm of is at the left side. (e) A schematic figure of the molecular machine. When the arm is at the right side. Only the arm after the joint is shown.
- Fig. 27-4. A ligand pool used in the machine learning by Janet et al. (2018).
- Fig. 27-5. The palladium-catalyzed Buchwald-Hartwig cross-coupling reaction.
- Fig. 27-6. Experimental design and analysis (a) Multidimensional discovery of catalytic coupling reactions. (b) An alkyne hydroallylation and a nickel-catalyzed variant of alkyne diarylation.
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PREFACE

In this book, topics of organic chemistry are not separated from those of inorganic chemistry. This has not been done before. Most organic chemistry topics appear from section twelve (Zr, Hf, and Ta) to section sixteen (Pd and Pt), because these elements form new complexes and work as catalysts for reactions in organic chemistry.

Part Four discusses specific topics not included in Parts One, Two, and Three. These topics include catalysts for cars (section nineteen), anti-Markovnikov reactions (twenty), zeolites and luminescence (twenty-one), Perovskites materials (twenty-two), MOF materials (twenty-three), water harvesting and purification (twenty-four), functional polymers (twenty-five), artistic molecules (twenty-six), molecular machines (twenty-seven), and ecological topics (twenty-eight).

You will notice that this book discusses materials science in terms of industrial, inorganic, and organic chemistry, but contains only a few mentions of biochemistry or life-related-sciences, which form a large proportion of this field today. Of course, this can be inferred from the title, and the author intentionally removed such topics because these topics have been summarized in another of the author's books, *Biochemistry in Materials Science: Catalysts, Complexes and Proteins* (Makishima, 2018). The books, therefore, act as a companion to each other.

Index of periodic tables.

A. Part One, Two and Three (Sections from One to Eighteen)

$H_{1,2}^1$	ELEMENT ^{Main} _{Sub} Section number																He^2
$Li_{3,4,6,10}^3$	Be^4															$F_{4,9}^{10}$	Ne^2
$Na_{2,9}^5$	$Mg_{4,8,10}^2$															$O_{8,9}^{10}$	Ar
$K_{3,4,10,15,18}^5$	$Ca_{2,10,14}^3$	Sc_{14}	$Ti_{1,4}^{11}$	$V_{1,11}$	Cr_6^{11}	$Mn_{7,11,14}$	$Fe_{3,8,11}$	$Co_{3,8,10,11}$	$Ni_{3,8,9,11}$	$Cu_{4,9,11,15,16}$	$Zn_{3,7,10,12,14,17}$	$Ga_{7,8,8}^3$	Ge_8^3	As^8	$Se_{9,13}^8$	Kr	
Rb^5	Sr	Y^{18}	$Zr_{4,8,12,16}$	Nb_{10}	$Mo_{9,11,13}$	Tc	$Ru_{9,14}$	$Rh_{10,15}$	$Pd_{8,10,13,16}$	$Ag_{13,16,17}$	$Cd_{9,11}$	In_6^4	$Sn_{10,18}$	$Sb_{9,16,18}$	$Te_{9,9}$	Xe^{10}	
Cs^5	Ba	L	$Hf_{4,12}$	$Ta_{10,12}$	$W_{4,8,13}$	Re	Os^{14}	$Ir_{5,11,15}$	$Pt^{16,17,18}$	$Au_{9,16,17}$	Hg^{17}	Tl_8	$Pb_{1,2,8,9,17}$	Bi_8^8	Po	Rn	
Fr	Ra	A	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

B. Part Four (Sections from Nineteen to Twenty-eight)

$H_{2,28}^4$	ELEMENT ^{Main} _{Sub} Section number																												He
Li	Be																											Ne	
$Na_{2,28}^3$	Mg_{25}^2																											F_{24}^{24}	Ar
K_{28}^3	Ca	Sc	Ti	V	Cr_{14}	Mn	Fe_{26}	Co^{24}	$Ni_{24,27}$	$Cu^{1,23,26}$	Zn^{23}	Ga	Ge	As^{26}	Se	Kr													
Rb	Sr^{21}	Y	$Zr_{19,24}$	Nb	Mo	Tc	$Ru^{19,20,26}$	Rh^{19}	$Pd^{19,20,26,27}$	$Ag^{1,23}$	Cd^{24}	In	Sn^{26}	Sb	Te	Xe													
Cs	Ba	L	Hf	Ta	W^{24}	Re	Os	Ir	$Pt^{19,20}$	Au^{21}	Hg^{24}	Tl	$Pb^{22,24}$	Bi	Po	Rn													
Fr	Ra	A	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og												
Li	La	Ce^{19}	Pr^{19}	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu														
A	Ac	Th	Pa	$U^{23,28}$	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr														

The author was once a pure materials-scientist in a company. Then he became an analytical geochemist in the Institute for Study of the Earth's Interior (ISEI), Okayama University at Misasa, which has been recently renovated into the Institute for Planetary Materials (IPM). He achieved his professorship in 2006 in ISEI, and he has published over 60 scientific papers. He had to give up research activities at 55 years old because of his health problems, and so he became an author of modern sciences. He has already published three books: *Thermal Ionization Mass Spectrometry (TIMS): Silicate Digestion, Separation and Measurement* (Makishima 2016); *Origins of the Earth, Moon, and Life: An Interdisciplinary Approach* (Makishima 2017); and *Biochemistry in Materials Science: Catalysts, Complexes and Proteins* (Makishima 2018). This is his fourth book. These books represent his wide interests in science. The author is very much fascinated by the beauty of inorganic materials, as well as biochemical materials, especially the chemical formulae of inorganic complexes as described in section twenty-six of this book.

References

- Makishima, Akio. 2016. *Thermal ionization mass spectrometry (TIMS). Silicate digestion, Separation, Measurement*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.
- Makishima, Akio. 2017. *Origins of the Earth, Moon and Life: a Multidisciplinary Approach*. Amsterdam: Elsevier.
- Makishima, Akio. 2018. *Biochemistry in Materials Science: Catalysts, complexes and proteins*. Amsterdam: Elsevier.

PART ONE:
TOPICS FOR TYPICAL ELEMENTS

SECTION ONE

PHYSICAL CONSTANTS AND HYDROGEN RELATED TOPICS

Chapter 1.1. The new proton's atomic mass

Heiße et al. (2017) reported the precise measurement of a single proton's atomic mass with a purpose-built Penning-trap system. A comparison with the previous data is shown in Fig. 1-1.

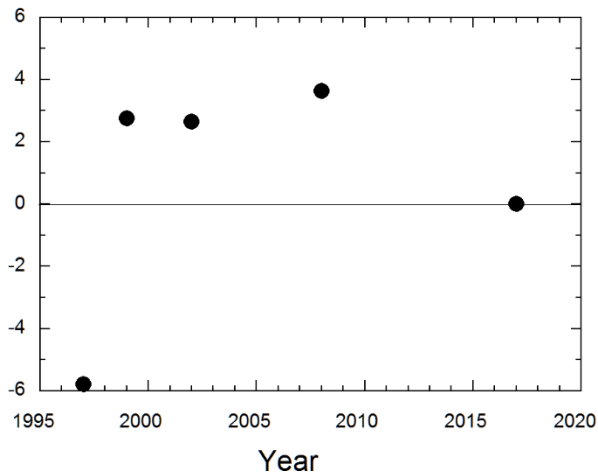


Fig. 1-1.