

# BIOINORGANIC CHEMISTRY

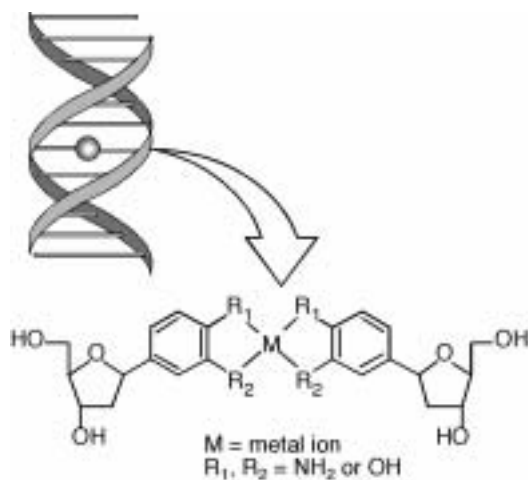
## Annual Research Review

### (1) “Toward Nano-Assembly of Metals through Engineered DNAs”

Replacement of the hydrogen-bonded base pairing of natural DNA by alternative base pairing modes is expected to lead not only to expansion of the genetic alphabet but to novel DNA structures and functions based on the controlled and periodic spacing of the building blocks along the helix axis. Recently we envisioned the use of charged or uncharged metal complexes as replacement building blocks in the interior of the DNA helix. Our approach for the incorporation of metal complexes into the DNA framework is based on the direct modification of a DNA base itself, turning it into a metal-chelating nucleobase wherein two nucleobases are paired through metal coordination. We reported that the introduction of metal-assisted base pairs directed towards what we term the nano-assembly of metals into the interior of the DNA helix. Specifically, we detailed the syntheses of artificial  $\beta$ -C-nucleosides bearing a chelator nucleobase (*o*-phenylenediamine, catechol, or 2-aminophenol), their metal coordination properties with metal ions, and the incorporation of these building blocks into DNA oligomers. These results raise the appealing possibility that this approach could lead eventually to a novel molecular architecture-type approach to the nano-assembly of multi-metal arrays.

A-1) *Eur. J. Pharm. Sci.*, **13**, 77-83 (2001)

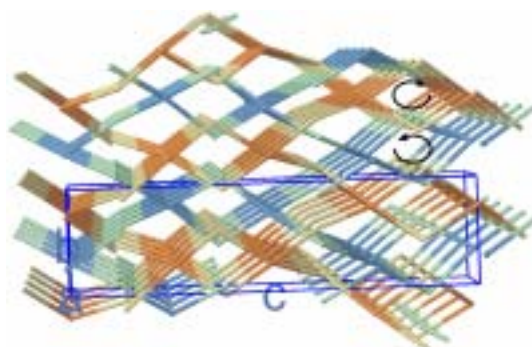
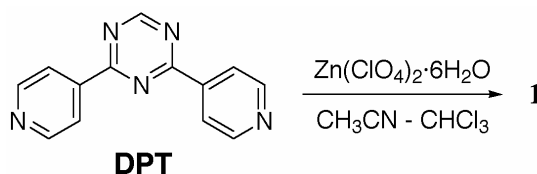
A-8) *Supramol. Chem.*, **13**, 671-675 (2001)



### (2) “Spontaneously Resolved Chiral Interpenetrating 3-D Nets with Two Different Zinc Coordination Polymers”

A net-based approach to metal coordination polymers using ligands with a range of proper geometries and connectivities has been expected to develop new functionalized materials with useful electronic, magnetic, electrochemical, optical, or catalytic properties. 2,4-Di-(4-pyridyl)-1,3,5-triazine (DPT), an angular dipyrindine ligand, has attracted our attention in connection with structural control of discrete or divergent coordination networks. This ligand could potentially provide both discrete and divergent products upon metal complexation under appropriate conditions. We reported the synthesis and X-ray crystal structure of a novel zinc-DPT coordination polymer **1** which consists of an interpenetrating pair of 3-D nets of different composition (FIG. 1). The most striking feature of this complex is that each single crystal is spontaneously resolved in the solid state. Such completely stereospecific self assembly without any chiral auxiliary in self-assembly would offer a useful tool for chiral molecular recognition and asymmetric catalysis.

A-12) *J. Am. Chem. Soc.*, **123**, 10750-10751 (2001)



**FIG. 1** A view of the doubly interpenetrating nets in complex **1**.

# 生物無機化学研究室

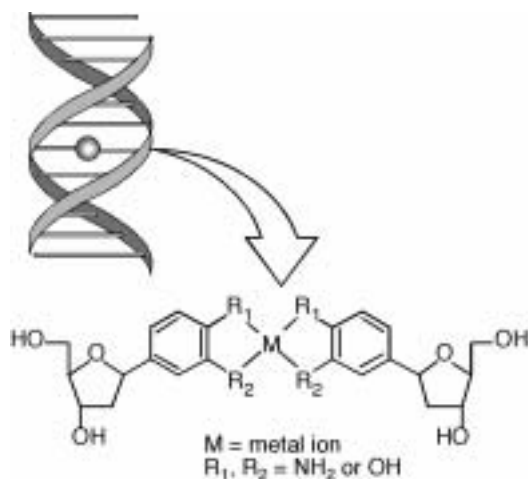
## 研究レビュー

### (1) 人工 DNA を用いた金属のナノ集積化に向けて

天然 DNA の水素結合型塩基対を他の塩基対様式に置き換えることは、遺伝子アルファベットの拡張ばかりでなく、ビルディングブロックがらせん軸に沿って制御された形で周期的に並ぶことに基づく、DNA の新しい構造や機能の構築につながる。最近我々は、電荷をもつ(あるいはもたない)金属錯体を DNA の内部に配列することに着目した。DNA の骨格構造に金属錯体を導入するというこのアプローチは、DNA 塩基そのものを直接化学修飾することに基づいている。すなわち、DNA 塩基を金属配位型の塩基に置き換え、金属イオンにより塩基対を形成させようというものである。DNA の内部に金属をナノ集積化することを指向し、オルトフェニレンジアミン、カテコール、あるいは 2-アミノフェノールを核酸塩基とする人工 *C-C*-ヌクレオシドの合成方法を確立し、それらと金属イオンとの相互作用、DNA オリゴマーへの導入方法について詳しく検討した。本研究成果は、金属イオンの秩序配列化のための新しい分子構築法を提供するものである。

A-1) *Eur. J. Pharm. Sci.*, **13**, 77-83 (2001)

A-8) *Supramol. Chem.*, **13**, 671-675 (2001)



### (2) 二つの異種亜鉛ポリマーから成る相互貫入型三次元錯体とその自然分晶

適当なジオメトリーと結合性をもった配位子を用いて、編み目構造型金属配位ポリマーを構築するアプローチは、有用な電子的、磁氣的、電気化学的、

光学的、触媒機能をもつ新しい機能性材料につながる事が期待される。直角構造をもつジピリジン型配位子である、2,4-Di-(4-pyridyl)-1,3,5-triazine (DPT) は、金属錯体の分子量を制御するという観点(すなわち、分子量の定まった集積型金属錯体ができるか、無限型の金属ポリマーができるかという観点)から、魅力的な分子である。この配位子は、金属イオンの存在下で、条件によってはどちらも構築できる可能性を秘めている。我々は、DPTの亜鉛錯体1の合成とX線結晶構造解析を行い、その結果、亜鉛錯体1は異なる組成をもつ二つの三次元ネットが相互貫入する構造をもつことが明らかになった(FIG. 1)。また、それぞれの単結晶は固体状態で自然分晶していることがわかった。このような、アキラルな配位子からキラルな集積型金属錯体への自己集積化は、不斉分子認識や不斉触媒の新しい手法を開発する上で重要な知見を与えるであろう。

A-12) *J. Am. Chem. Soc.*, **123**, 10750-10751 (2001)

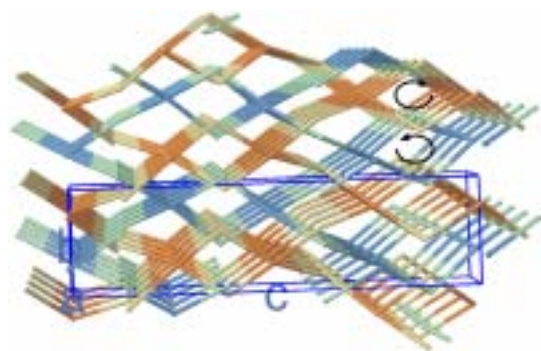
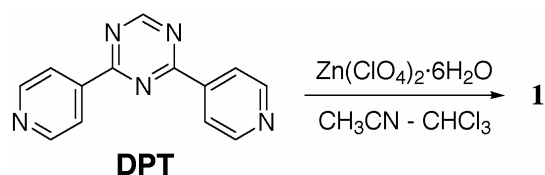


FIG. 1 A view of the doubly interpenetrating nets in complex 1.

## A. Original Papers

- 1) K. Tanaka, (M. Tasaka), (H. Cao) and M. Shionoya: "An Approach to Metal-Assisted DNA Base Pairing: Novel  $\beta$ -C-Nucleosides with a 2-Aminophenol or a Catechol as the Nucleobase", *Eur. J. Pharm. Sci.*, **13**, 77-83 (2001).
- 2) (K. Yamaguchi), (F. Akagi), (S. Fujinami), (M. Suzuki), M. Shionoya and (S. Suzuki): "Hydrolysis of Phosphodiester with Hydroxo- or Carboxylate-Bridged Dinuclear Ni(II) and Cu(II) Complexes", *Chem. Commun.*, 375-376 (2001).
- 3) (H. Kurosaki), (H. Yoshida), (A. Fujimoto), (M. Goto), M. Shionoya, (E. Kimura), (E. Espinosa), (J.-M. Barbe) and (R. Guillard): "Synthesis and Crystal Structures of Palladium(II) Complexes of 1,11-Bis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione", *J. Chem. Soc., Dalton Trans.*, 441-447 (2001).
- 4) (X.-H. Bu), (M. Du), (L. Zhang), (D.-Z. Liao), (J.-K. Tang), (R.-H. Zhang) and M. Shionoya: "Novel Nickel(II) Complexes with Diazamesocyclic Ligands Functionalized by Additional Phenol Donor Pendant(s): Synthesis, Characterization, Crystal Structures and Magnetic Properties", *J. Chem. Soc., Dalton Trans.*, 593-598 (2001).
- 5) (X.-H. Bu), (M. Du), (L. Zhang), (Z.-L. Shang), (R.-H. Zhang) and M. Shionoya: "Novel Copper(II) Complexes with Diazamesocyclic Ligands Functionalized by Additional Donor Group(s): Syntheses, Crystal Structures and Magnetic Properties", *J. Chem. Soc., Dalton Trans.*, 729-735 (2001).
- 6) (X.-H. Bu), (M. Du), K. Tanaka, M. Shionoya and (M. Shiro): "Nickel-Mediated Alcoholysis Reaction of Carbon-Nitrogen Triple Bond: Structural Characterization of an Unprecedented Moisture Stable Imido Ester with a Single *E*-Configuration", *Inorg. Chem. Commun.*, **4**, 150-152 (2001).
- 7) (X.-H. Bu), (M. Du), (Z.-L. Shang), (L. Zhang), (Q.-H. Zhao), (R.-H. Zhang) and M. Shionoya: "Novel Diazamesocyclic Ligands Functionalized with Pyridyl Donor Group(s) - Synthesis, Crystal Structures, and Properties of Their Copper(II) Complexes", *Eur. J. Inorg. Chem.*, **4**, 1551-1558 (2001).
- 8) (M. Tasaka), K. Tanaka, (M. Shiro) and M. Shionoya: "A Palladium-Mediated DNA Base Pair of a  $\beta$ -C-Nucleoside Possessing a 2-Aminophenol as the Nucleobase", *Supramol. Chem.*, **13**, 671-675 (2001).
- 9) (X.-H. Bu), (H. Liu), (M. Du), (K. M.-C. Wong), (V. W.-W. Yam) and M. Shionoya: "Novel Box-like Dinuclear or Chain Polymeric Silver(I) Complexes with Polypyridyl Bridging Ligands: Syntheses, Crystal Structures, Spectroscopic and Electrochemical Properties", *Inorg. Chem.*, **40**, 4143-4149 (2001).
- 10) (X.-H. Bu), (M. Du), K. Tanaka, M. Shionoya and (M. Shiro): "Novel Crystals as Candidates for Frequency Up-Converted Materials: Syntheses and Crystal Structures of Two Trogers's Bases", *J. Chem. Res.*, 243-245 (2001).
- 11) (X.-H. Bu), (W. Chen), (S.-L. Lu), (R.-H. Zhang), (D.-Z. Liao), (W.-M. Bu), M. Shionoya, (F. Brisse) and (J. Ribas): "Flexible meso-Bis(sulfinyl) Ligands as Building Blocks for Copper(II) Coordination Polymers: Cavity Control by Varying the Chain Length of Ligands", *Angew. Chem. Int. Eng.*, **40**, 3201-3203 (2001).
- 12) M. Sasa, K. Tanaka, (M. Shiro), (X.-H. Bu) and M. Shionoya: "Spontaneously Resolved Chiral Interpenetrating 3-D Nets with Two Different Zinc Coordination Polymers", *J. Am. Chem. Soc.*, **123**, 10750-10751 (2001).

## D. Books

- 1) 塩谷光彦: 「イオン性液体・デザインで広がるその機能」, 化学, 東京化学同人, **56**(5), 12-16 (2001).
- 2) 塩谷光彦: 「金属イオンで結合する人工 DNA」, 総研大ジャーナル, No. 0, 40-45 (2001).
- 3) 塩谷光彦: 「イオン性液体と生命化学の接点」, 酵素工学ニュース, No. 46, 4-7 (2001).