Available online at www.sciencedirect.com
ScienceDirect
Coordination Chemistry Reviews 251 (2007) 2732–2742
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Programmable metal assembly on bio-inspired templates

Kentaro Tanaka [a,*], Mitsuhiko Shionoya [b,*]

[a] *Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*
[b] *Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Received 30 May 2007; accepted 20 August 2007
Available online 24 August 2007

Contents

1. Introduction 2732
2. Metal-mediated base pairing in DNA 2733
3. Structural control of DNA by metal-mediated base pairing 2734
4. Quantitative assembly of metal complexes into artificial DNA 2737
5. Programmable heterogeneous metal arrays on DNA templates 2739
6. Conclusions 2741
References 2741

Abstract

Besides the biological importance of DNA as genetic information storage and expression, DNA has great potential to act as a smart molecule for programmable self-assembly of functional units since it is possible to encode molecular assembled systems using sequences of nucleobases in a designable fashion. Recently, we have reported a novel base-pairing motif in DNA duplex that is based on the replacement of hydrogen-bonded base pairs by metal-mediated base pairs. This review covers our recent approaches to precise programming of metal arrays by means of artificial DNA templates.

Keywords: Assembled metal complexes; DNA; Self-assembly; Template synthesis

1. Introduction

The ultimate goal of nanoscience and nanotechnology is to arrange atoms and/or molecules precisely in three-dimensional space and to make it operate in a highly controlled way at the atomic levels. In view of the efficient construction of high-functional nanostructures and nanospaces, the precise assembly of metal complexes has been widely investigated. Approaches for molecular assemblage of metal complexes are classified as follows: (1) crystallization [1], polymeric self-assembly [2], and coordination polymer synthesis [3] (Fig. 1a) and (2) discrete self-assembly such as multinuclear metal complexes with stiff multidentate ligands [4], step-by-step elongation of metal complexes or template ligands [5] (Fig. 1b). However, dispersion of products in the number and the sequence of assembled complexes is inherent in the former approaches (1) that can assemble a large number of components at a time, and the latter discrete self-assembly approaches (2) are still far from extension to treating a large number of components. On the other hand, biological system generates biopolymers such as DNA, protein, and polysaccharide without any dispersion in "number", "composition", "sequence", and "direction". These molecules organize with highly "selective" and "specific" spatial arrangement. Hence, the structural motifs of biopolymers, which have been optimized by evolution over several billion years, have great potential as functional templates for programmable self-assembly to generate well-defined molecular architectures. Especially, the double-helical DNA molecule is competent to serve as a nanoscale material. The diameter of DNA is about 2 nm, its helix contains coaxially stacked base pairs separated by 3.4 Å with each other, and its helical pitch is about 3.4 nm for typical right-handed B-DNA (Fig. 2a). Furthermore, automated DNA synthesis allows quick and easy access to any desired

* Corresponding authors.
E-mail addresses: kentaro@chem.nagoya-u.ac.jp (K. Tanaka), shionoya@chem.s.u-tokyo.ac.jp (M. Shionoya).

0010-8545/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2007.08.018

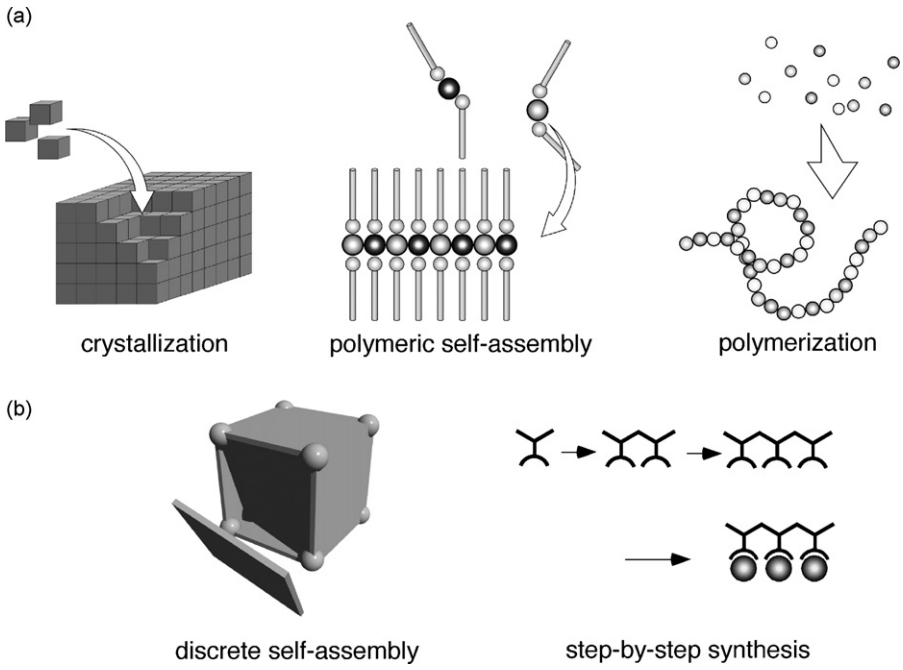


Fig. 1. Molecular assemblage of metal complexes: (a) polymeric approaches and (b) discrete approaches.

sequence of DNA. Herein, this review highlights precisely controlled assembly of metal complexes on DNA templates towards functionalized materials including our recent research progress (Fig. 2b).

2. Metal-mediated base pairing in DNA

In nature, most of the biological information is stored on DNA as base sequences consisting of only four kinds of nucleobases. The most important characteristic of DNA is sequence architecture of nucleobases and its structural hierarchy. The synthetic strategies for DNA strands have been established and sophisticated for over 30 years [6]. Nowadays, automated DNA synthesizers can routinely make oligomers in length approaching 100 nucleotides, and also enzymatic tools developed for biotechnology can be employed to elongate and amplify DNA strands without loss of programmed information recorded as sequences of nucleobases. Automated DNA synthesizers are applicable not only to natural nucleotides, but also to artificial building blocks that have two hydroxy groups protected by a dimethoxytrityl (DMTr) group for one and a phosphoramidite group for the other (Fig. 3) to be incorporated into oligonucleotides with meaningful sequences. Thus, the basic structural motifs of DNA have been extended to encode precise molecular assembled systems [7–13]. Recently, a few examples have been reported for incorporation of dye molecules or metal complexes into DNA scaffolds instead of hydrogen-bonded base pairs directed towards photonic or electronic wires [14–16]. Alternative non-natural base pairs have been extensively studied to expand genomic alphabets for extension of genomic information [17]. Along this line, we have developed metal-mediated base pairing instead of hydrogen bonded one, thereby creating a novel base-pairing motif in duplex DNA (Fig. 4) [13,18]. The artificial DNA with metal ligands instead of canonical nucleobases was expected to form double helical structure through metal-mediated base pairing in the presence of appropriate metal ions. Actually, metal ions could be arrayed in the center of the duplex site-selectively along with the designable sequences of the ligand-type nucleotides. Also combinatorial optimization with a metal ion and a metal ligand allows fine tuning of selectivity and characters of metal complexes in terms of (1) a variety of coordination number and geometry, (2) thermodynamics and kinetics of binding and dissociation, and (3) physical and chemical properties such as redox-, magnetic-, optical-, and radio-activities and Lewis acidity.

We have reported the first example of a metal-mediated base pair consisting of the artificial nucleosides **1** in which bidentate ligand, *o*-phenylenediamine, is introduced as a ligand for a 2:1 planar complex with a Pd^{2+} ion. The resulting complex is structurally analogous in shape and size with natural hydrogen-bonded base pairs [19]. Since then, we [19–24] and others [25–30] have reported many examples of metal ligands as DNA-base substitutes using a monodentate (**5**, **14**), bidentate (**1**–**4**, **6**–**10**), tridentate (**11**–**13**), hard-donor (**3**, **4**, **11**) or soft-donor (**13**) ligand attached to a β-*N*- or a β-*C*-nucleoside skeleton (Fig. 5).

Appropriate combination of the artificial nucleosides with a metal ion allows formation of stable metal-mediated base pairs which could be incorporated into higher-order DNA structures at pre-determined positions (Fig. 6). Among these metal-mediated base pairs, a square-planar or a linear metal complex, the abovementioned Pd^{2+}-mediated base pairing with 2-amino-phenol [21], Ag^{+}-assisted base pairing with pyridine (**P**–Ag^{+}–**P**) [22], and Cu^{2+}-mediated base pairing with hydroxypyridone (**H**–Cu^{2+}–**H**) [23], have a geometrically analogous motif of H-bonded natural base pair. Alternatively,

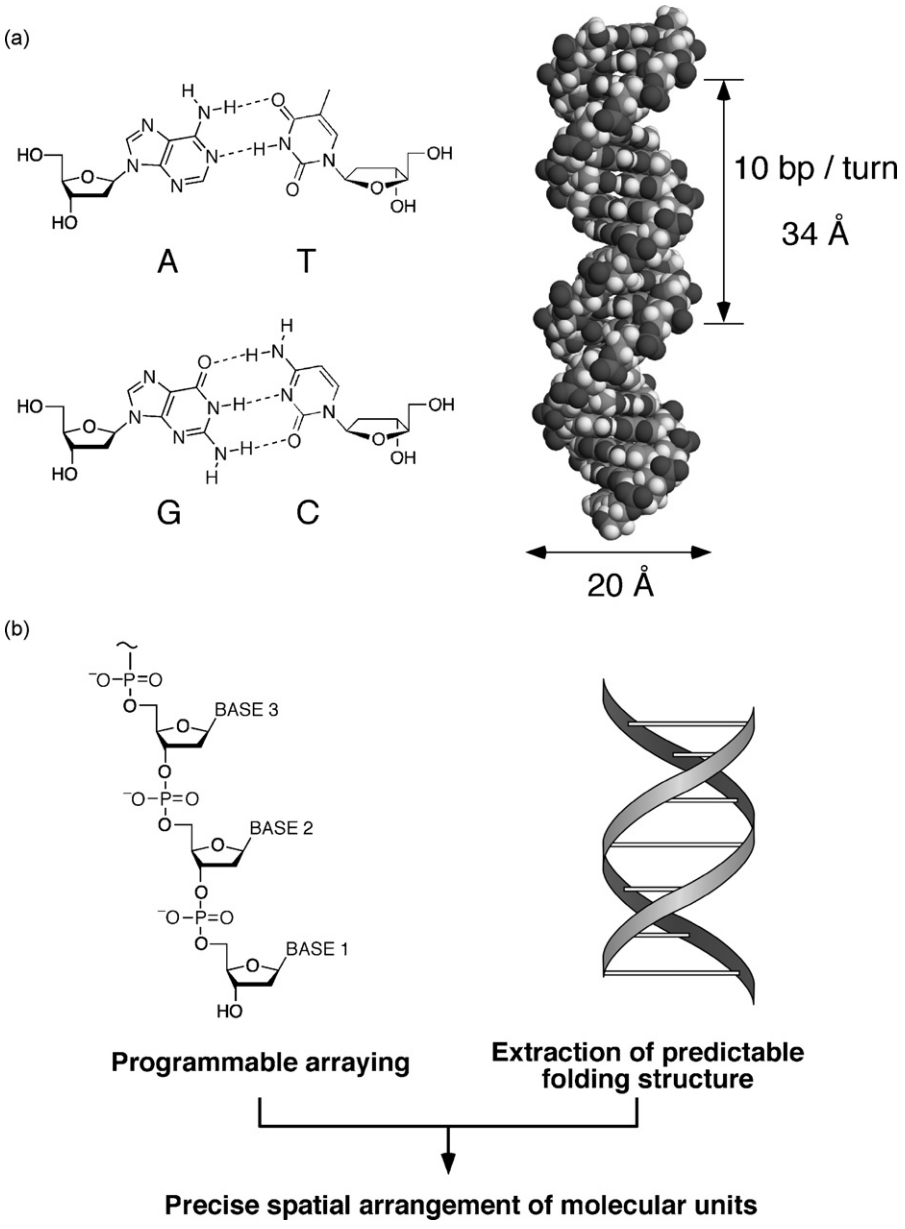


Fig. 2. (a) DNA structure and (b) precise molecular assembly inspired by DNA.

distorted non-planar base pairs such as a B^{3+}-induced base pair with catechol [20] could be incorporated into DNA higher ordered structures. Other groups have also reported metal-mediated base pairs such as a Cu^{2+}-mediated heterogeneous [1 + 3]-type base pair between pyridine and pyridine-2,6-dicarboxylate or pyridine-2,6-dicarboxamidate [25a,b and d], an Ag^{+}-mediated one with 2,6-bis(methylthiomethyl)pyridine bases [25c], a Cu^{2+}-mediated bipyridine-base pair [26], Ni^{2+}-mediated pyridylpurine- and pyridylpyrimidinone-base pairs [28], and an Ag^{+}- or Hg^{2+}-mediated imidazole-base pairs [30]. Salicylic aldehyde (**S**)-bearing oligonucleotides were also reported which was tremendously stabilized by addition of ethylenediamine (en) and metal ions such as Cu^{2+}, Mn^{2+}, Fe^{2+} and VO^{2+} which lead to the formation of an interstrand salen-complex like **S**–Cu^{2+}(en)–**S** through a covalent cross linking with ethylenediamine [29] (Fig. 7). On the other hand, metal-mediated base pairing of a natural nucleobase has been reported. Two thymine bases in the deprotonated form coordinate to an Hg^{2+} ion to form a stable 2:1 complex [31,32]. The net charges and coordination geometries of the resulting metal complexes are important factors determining distinctive property of each metal array formed in DNA.

3. Structural control of DNA by metal-mediated base pairing

Bond energy of metal coordination occupies an intermediate position between those of covalent bonding and non-covalent bonding such as H-bonding. Hydroxypyridone-bearing nucleoside **4** forms a sufficiently stable base pair with a Cu^{2+} ion in a 10^{-5} M range at pH 7 (Scheme 1). Stability of a metal-mediated base pair is closely related to structural factors of DNA and

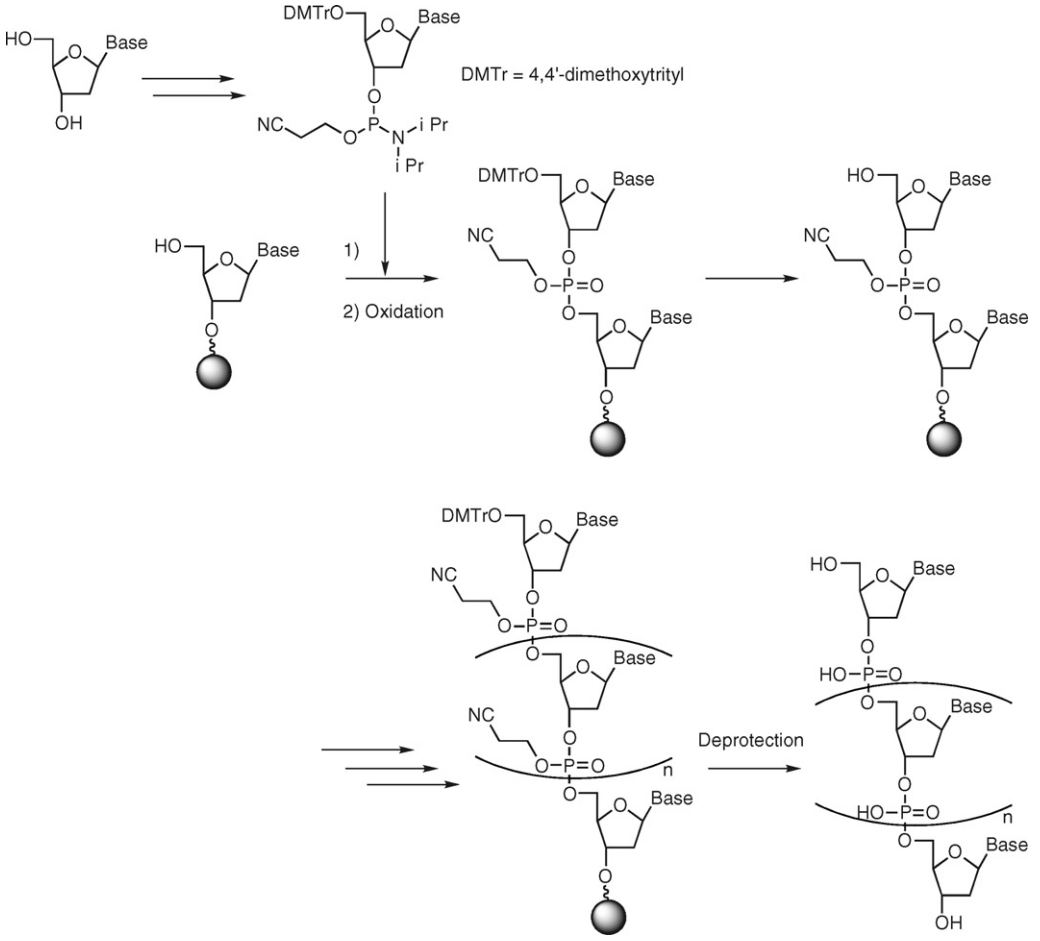


Fig. 3. Solid-state DNA synthesis (phosphoramidite method).

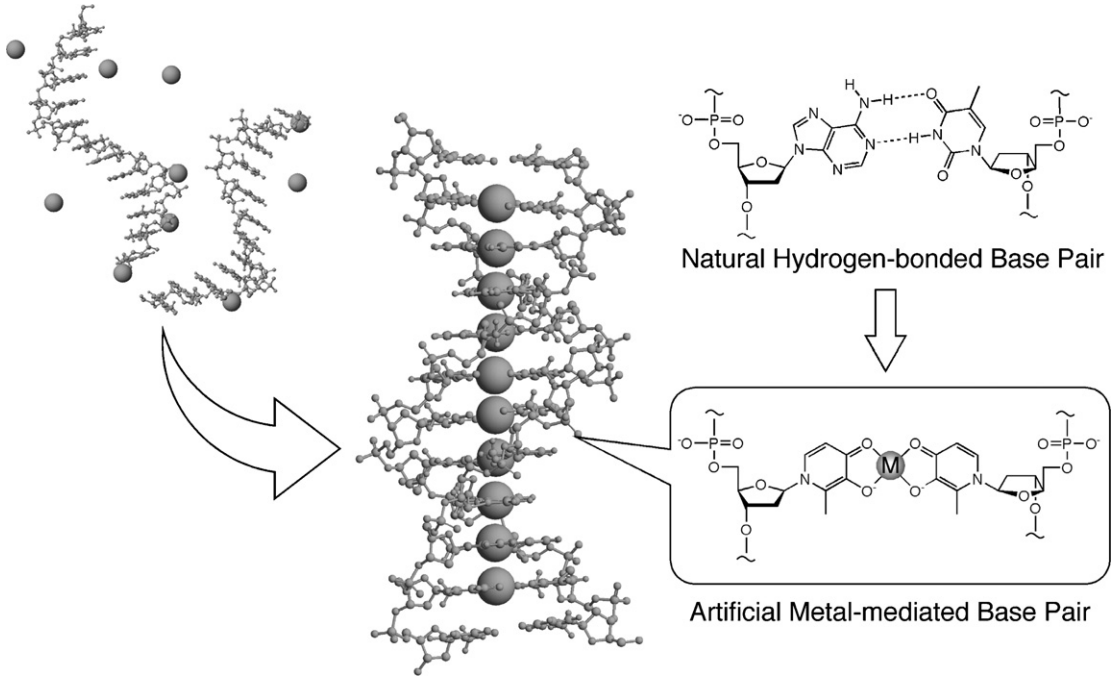


Fig. 4. An artificial DNA which has metallo-base pairs instead of hydrogen-bonded pairs.

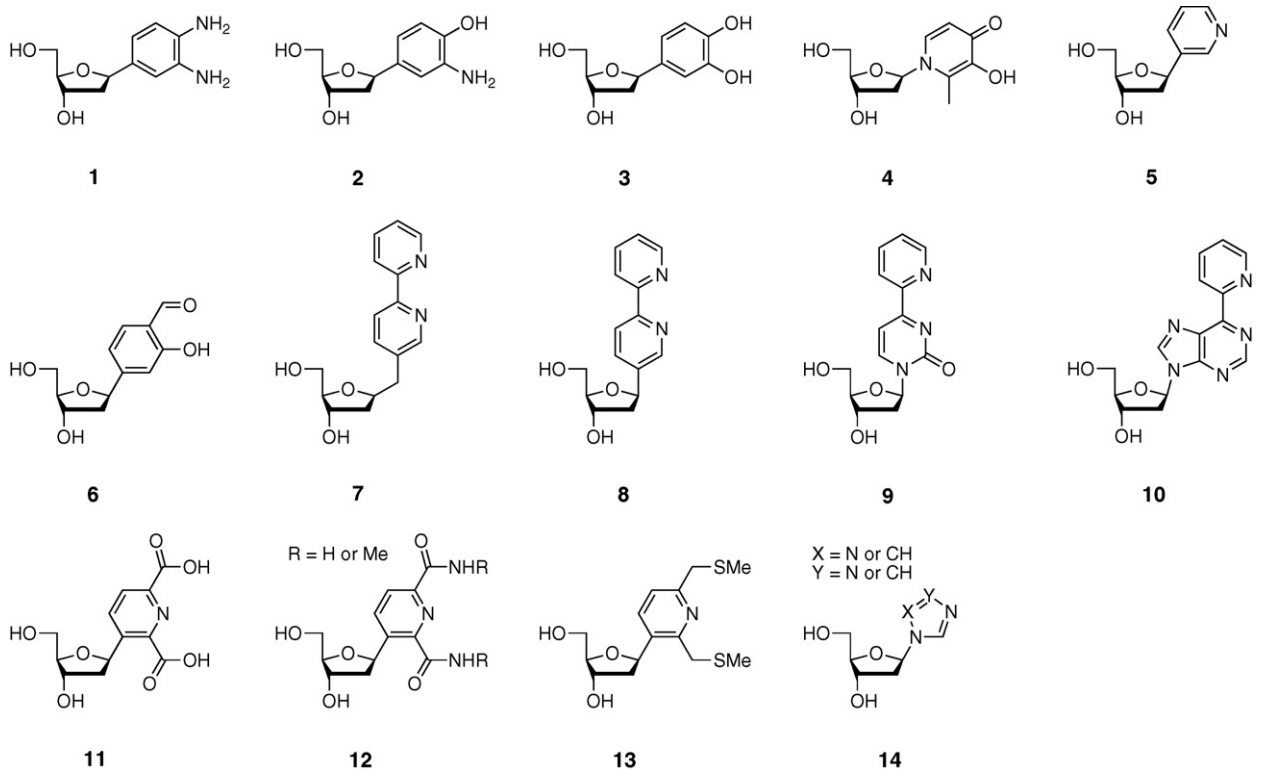


Fig. 5. Examples of artificial ligand-type nucleosides.

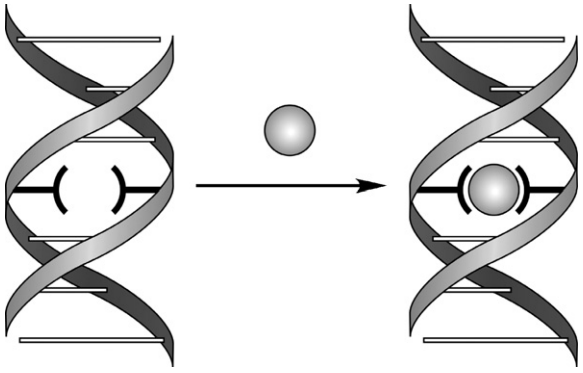
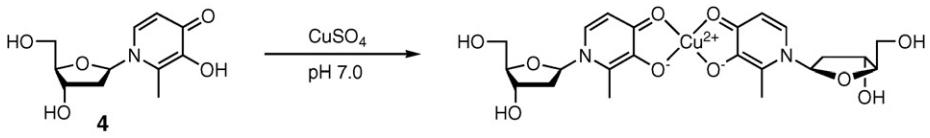


Fig. 6. Metal-induced duplex formation.

hydrophobic environment in the duplex structure. To examine the influence of metal-mediated base pairing on the thermal stability of a DNA double-stranded structure, an **H**–**H** pair was introduced in the middle of a 15-nucleotide DNA duplex (**15**) [23]. DNA double-strands thermally dissociate into a couple of single strands, and the melting temperature can be monitored by the hyperchromic shift at 260 nm. In the absence of Cu^{2+} ions, the duplex **15** showed a melting (denaturation) temperature of 37.0 °C (Fig. 8a), whereas a natural-type oligoduplex (**16**), in which the **H**–**H** base pair is replaced by an **A**–**T** base pair, denatured at 44.2 °C (Fig. 8b). Thus, in the absence of Cu^{2+}, the **H**–**H** base pair behaves as a mispair to destabilize the duplex. In contrast, addition of Cu^{2+} to the duplex **15** led to metal-mediated base pairing with higher thermal stability. Thermal denaturation of **15** in the presence of equimolar Cu^{2+} resulted in a biphasic melting curve with a melting point of 50.1 °C (Fig. 8c), which is higher than that of **15** in the absence of Cu^{2+}. Thus, the Cu^{2+}-assisted base pair, **H**–Cu^{2+}–**H**, stabilized the duplex by ca. 13 °C, whereas the natural duplex **16** remained nearly unaffected by addition of Cu^{2+} (Fig. 8d). Hence, transition between single strands and a double strand can be regulated by the formation of metal-mediated base pairing (Scheme 2) [23]. In the case of single-site incorporation of pyridine-bearing nucleosides in the middle of the sequence of oligo(dT·dA·dT) triple strand **17**, the thermal stability of triplex **17** was significantly increased by Ag^{+} complexation to form a base triplet (Scheme 3) [22].

Since the structural conversion of DNA is essentially relevant to duplication and transcription of genetic information, the strategy of the metallo-DNA would be an efficacious tool for manifestation of a gene.



Scheme 1.

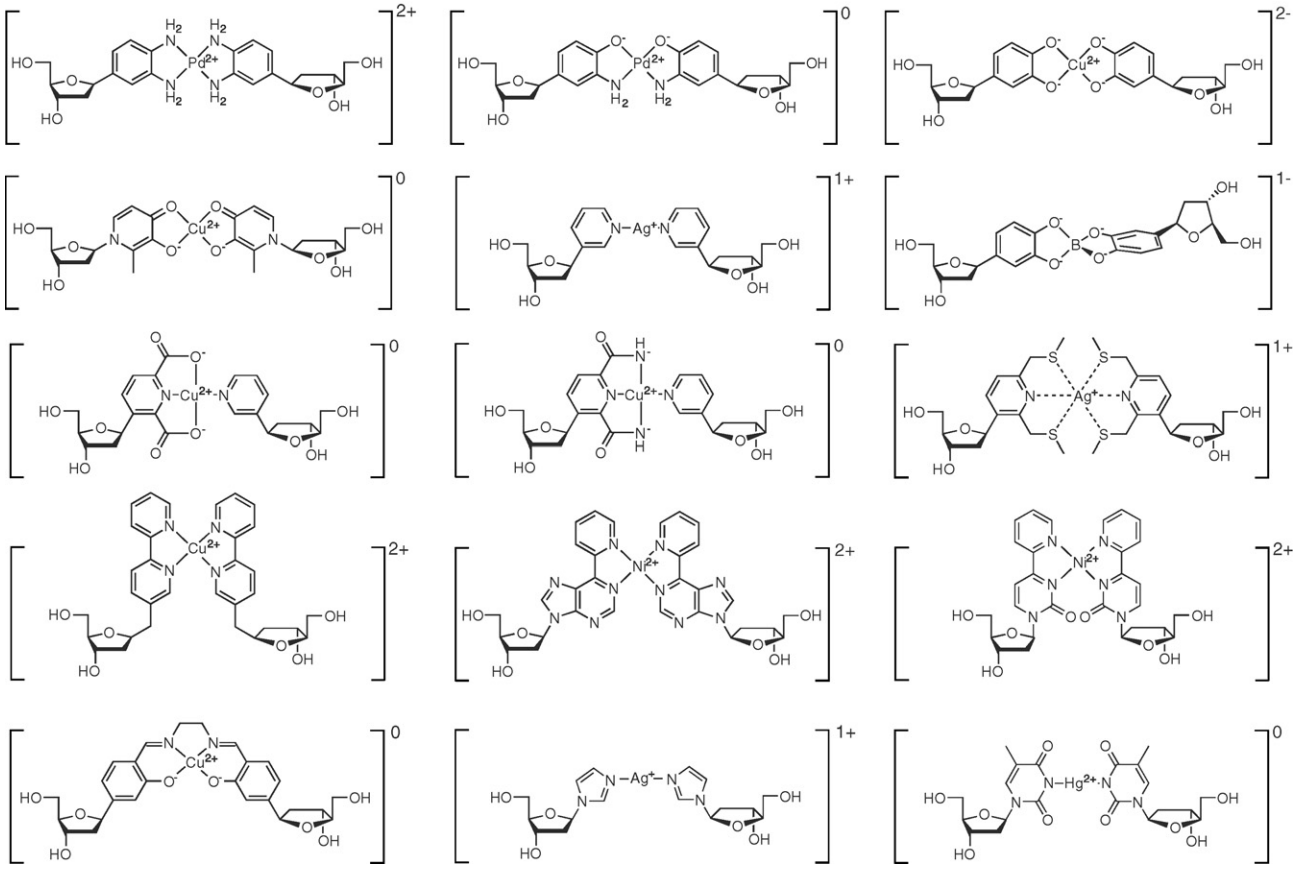
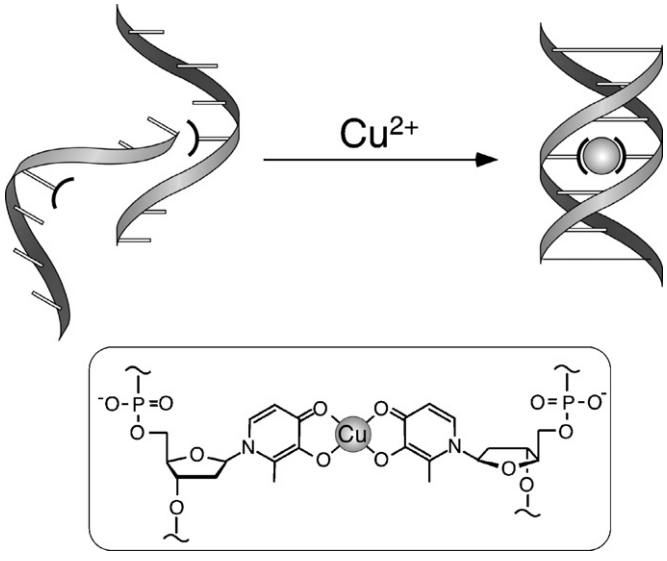


Fig. 7. Metal-mediated base pairs.



Scheme 2.

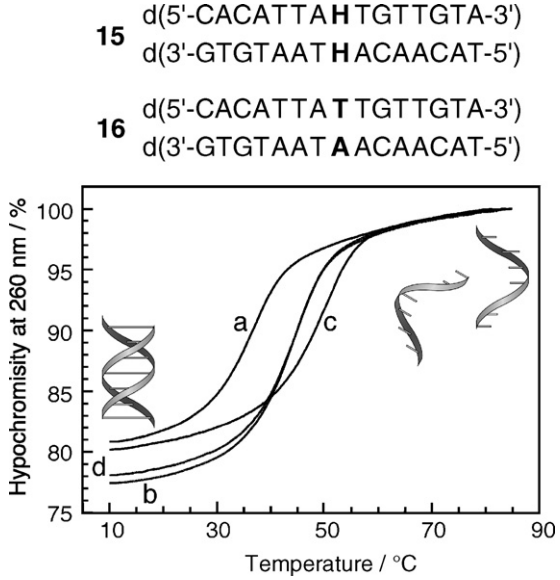
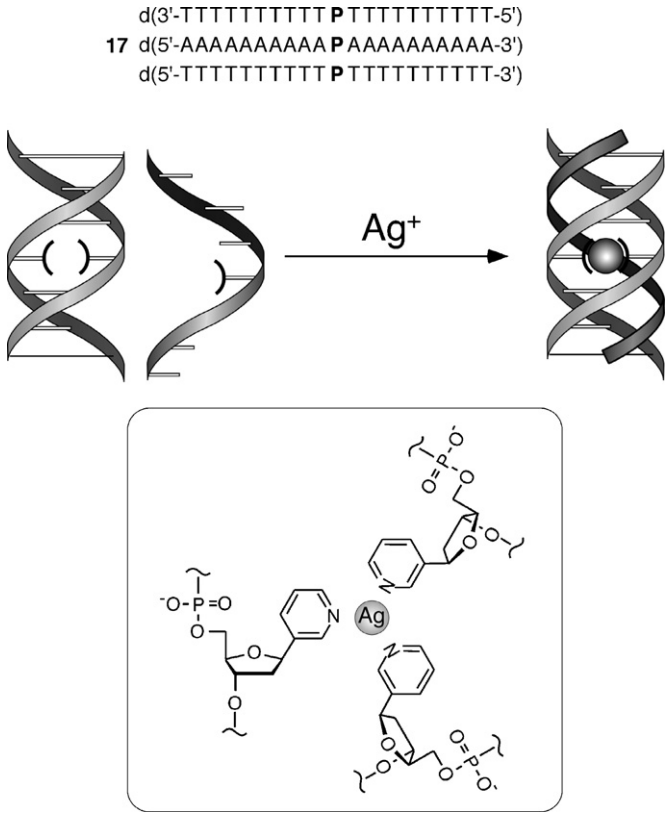


Fig. 8. Melting curves of the duplexes **15** (a and c) and **16** (b and d). [**15**] = [**16**] = 2.0 μM in 10 mM Sodium phosphate buffer, 50 mM NaCl (pH 7.0). [$CuSO_4$] = (a) and (b): 0 μM; (c) and (d): 2.0 μM.

4. Quantitative assembly of metal complexes into artificial DNA

Although crystallization has been one of the most powerful methodologies to array metal complexes, this is not suited to pre-design the number or the spatial arrangement of components. On the other hand, since DNA has a structural basis to array functionalized building blocks without any distribution of number and sequence, the artificial DNA could be a scaffold for one-dimensional arrays of a defined number of metal ions.



Scheme 3.

To array a predetermined number of Cu^{2+} complexes, we designed a series of artificial oligonucleotides, d(5′-G**H**$_n$C-3′) (n = 1–5), **18**–**22**, using hydroxypyridone nucleobases (**H**) as scaffolds of assemblage of Cu^{2+} (Fig. 9a) [33]. Fig. 9b shows the changes in the UV spectra of d(5′-G**H**$_5$C-3′)$_2$, **22**, with increasing amounts of Cu^{2+}. The absorbance at 280 nm derived from a hydroxypyridone moiety gradually decreased while a new peak at 307 nm appeared as the concentration of Cu^{2+} increases. The absorption spectra changed continually through two isosbestic points until the ratio of [Cu^{2+}]/[duplex] reached 5.0 through (Fig. 9b). This result clearly indicates five Cu^{2+} ions are quantitatively assembled into the duplex **22** *via* **H**–Cu^{2+}–**H** base pairing. Similar results were observed with the series of oligonucleotides, d(5′-G**H**$_n$C-3′) (n = 1–4). Overall, the changes in absorbance at 307 nm, plotted as a function of the ratio of Cu^{2+} to d(5′-G**H**$_n$C-3′)$_2$ (n = 1–5) (Fig. 9c), strongly suggested the duplex formation of Cu-n (n = 1–5) [where Cu-n (n = 1–5) denotes $n$$Cu^{2+}$·d(5′-G**H**$_n$C-3′)$_2$ (n = 1–5)] in which Cu^{2+}-mediated base pairs are aligned quantitatively in a direct stacked manner. The discrete structures were confirmed by electrospray ionisation time-of-flight mass spectrometry (ESI-TOF-MS). One to five Cu^{2+}-mediated base pairs of hydroxypyridone nucleobases have been systematically incorporated into the middle of template DNA duplexes, d(5′-G**H**$_n$C-3′)$_2$ (n = 1–5), in which unpaired d electrons on the Cu^{2+} ions arrayed in each complex couple ferromagnetically with one another in the stacked motives. An outline of a proposed right-handed, double-stranded structure with the quantitative formation of a magnetic chain inside the DNA is drawn in Fig. 10, where the Cu^{2+}–Cu^{2+} distance is 3.7 Å. This strategy

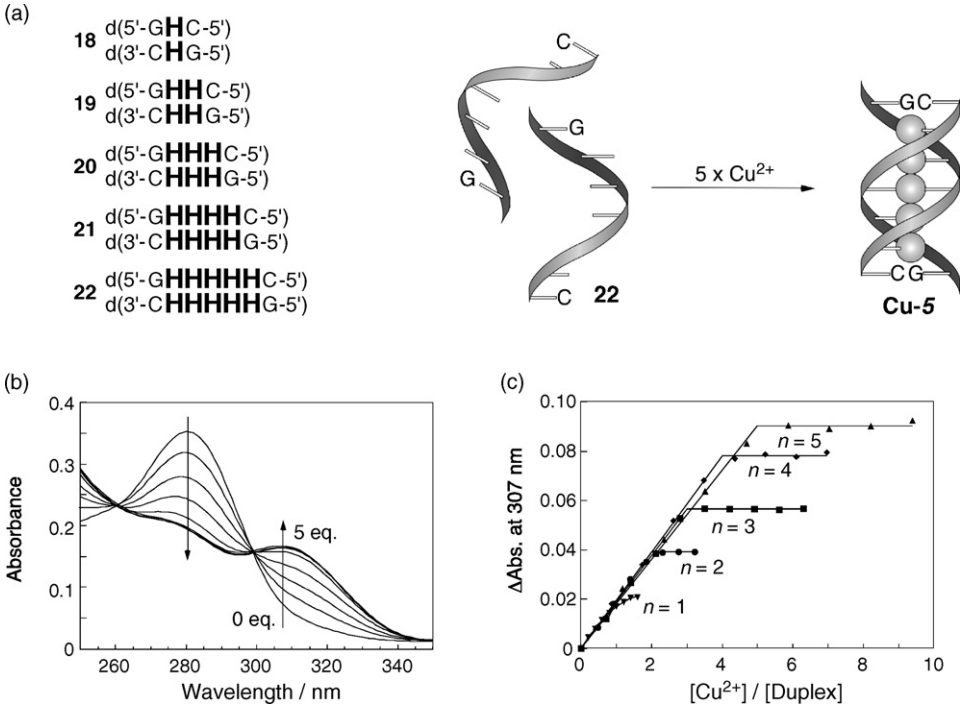


Fig. 9. Discrete metal assembly into the artificial DNAs: (a) template DNA strands; (b) photometric titration experiments of **21** at various concentrations of Cu^{2+} at 25 °C. [**21**] = 2.0 μM in 10 mM HEPES (pH 7.0) and 50 mM NaCl. (c) Plot of absorbance at 307 nm against the ratio of Cu^{2+} to **17**–**21**.

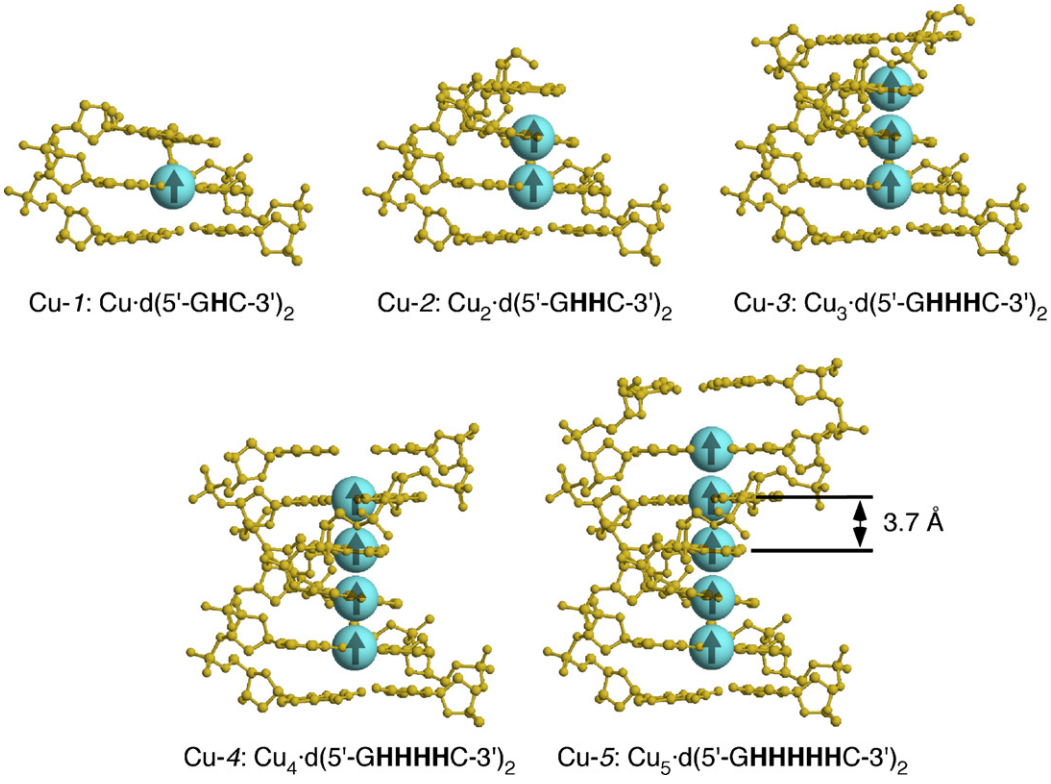
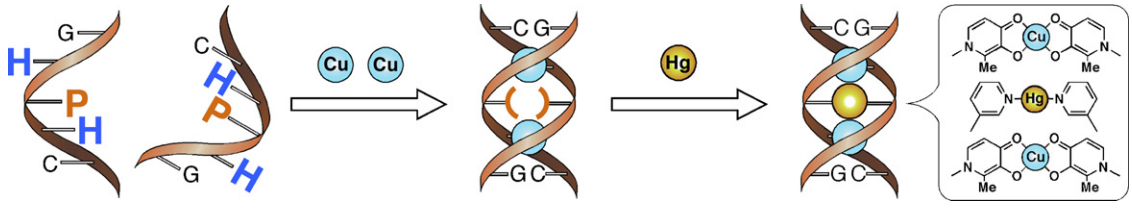


Fig. 10. Discrete spin arrays into the artificial DNAs.

represents a new method for metal arrays in solution in a discrete and predictable fashion, and for precise control of metal-metal electronic interactions, leading to the possibility of metal-based molecular devices such as molecular magnets and wires.

5. Programmable heterogeneous metal arrays on DNA templates

DNA acts as a smart molecule to assemble functional units since it is possible to use sequences of nucleobases to encode molecular assembled systems in a predetermined fashion. Sequencing of the ligand-type nucleotides on the artificial DNA strand would directly link to programmable arraying of heterogeneous metal ions on a DNA template. In order to investigate the possibility of stacking different metal ions on top of each other, a pentanucleotide d(5′-G**HPH**C-3′) was designed to array heterogeneous metal ions in a double helix, which contains two hydroxypyridone-bearing nucleotides (**H**) and one pyridine-bearing nucleotide (**P**) that prefers a linear complex with an Ag^+ or an Hg^{2+} ion (Scheme 4) [34]. Photometric titration experiments clearly demonstrated quantitative and site-selective formation of a trinuclear complex with two Cu^{2+} ions and one Hg^{2+} ion in the order, Cu^{2+}–Hg^{2+}–Cu^{2+} as programmed (Fig. 11). The pentanucleotide was found not to form duplex structures in the absence of Cu^{2+} or Hg^{2+} under the operating conditions, whereas photometric titration experiments using the pentanucleotide in the presence of Cu^{2+} clearly demonstrated Cu^{2+}-mediated duplex formation. As homogeneous metal arraying, the UV absorption around 278 nm arising from the hydroxypyridone moiety at 278 nm gradually decreased with increasing concentrations of Cu^{2+}, while a new peak appeared at 310 nm with two isosbestic points in the range of [Cu^{2+}]/[duplex] from 0.0 to 2.0 (Fig. 11a). The simultaneous change is ascribable to the deprotonation of phenolic hydroxy groups of hydroxypyridone ligands upon Cu^{2+} complexation [23]. Two Cu^{2+} ions were thus assembled into a single duplex quantitatively through formation of a couple of **H**–Cu^{2+}–**H**



Scheme 4.

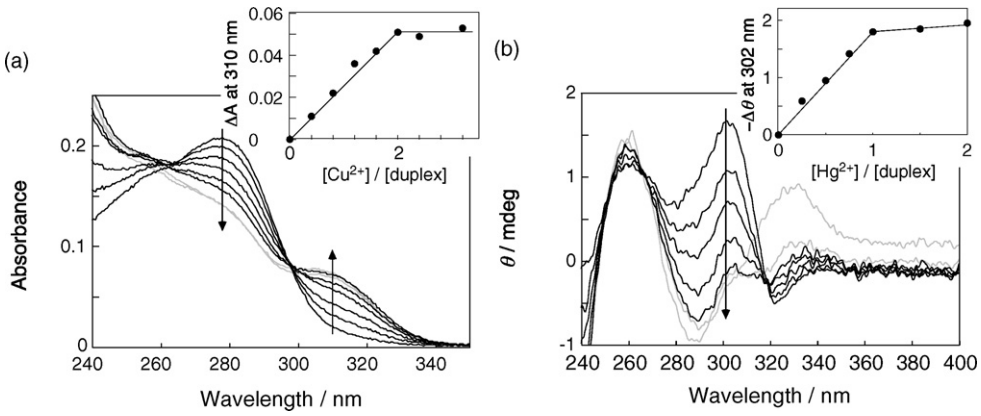


Fig. 11. Assemblage of Cu^{2+} and Hg^{2+} ions through duplex formation of d(5′-G**HPH**C-3′) [34]. (a) UV absorption changes of d(5′-G**HPH**C-3′) at various concentrations of $CuSO_4$ at 25 °C. [d(5′-G**HPH**C-3′)] = 4.2 μM in 10 mM HEPES (pH 7.0) and 50 mM $NaNO_3$ (inset: plot of absorbance changes at 310 nm against the ratio of Cu^{2+} to d(5′-G**HPH**C-3′)$_2$). (b) CD spectral changes of the duplex $2Cu^{2+}$·d(5′-G**HPH**C-3′)$_2$ at various concentrations of $Hg(NO_3)_2$ at 25 °C. [$2Cu^{2+}$·d(5′-G**HPH**C-3′)$_2$] = 2.1 μM in 10 mM HEPES (pH 7.0) and 50 mM $NaNO_3$ (inset: plot of circular dichroic changes at 302 nm against the ratio of Hg^{2+} to $2Cu^{2+}$·d(5′-G**HPH**C-3′)$_2$). A 1-cm path length quartz cell was used for scans from 400 to 240 nm at 25 °C.

base pairs. Subsequent incorporation of an Hg^{+} ion into each duplex was monitored by the circular dichroic (CD) analysis of the duplex at different concentrations of Hg^{2+} ions to verify the **P**–Hg^{2+}–**P** base pairing in the Cu^{2+}-mediated duplex (Fig. 11b). With an increase in the Hg^{2+} concentration, the positive Cotton effect at 302 nm gradually decreased linearly with the ratio of [Hg^{2+}]/[duplex] from 0.0 to 1.0. The heterogeneously metal-assembled structure was clearly demonstrated by ESI-MS measurements. This heterogeneous metal array is thermodynamically most stable and the complex structure consisting of five components (two DNA strands and three metal ions) spontaneously builds up in 100% yield. Similarly, an extended metal array, Cu^{2+}–Cu^{2+}–Hg^{2+}–Cu^{2+}–Cu^{2+}, was also successfully formed in the center of the duplex, d(5′-G**HHPHH**C-3′)$_2$ (Fig. 12).

The strategy for programmable metal arrays can be further extended by diverse ligand-type nucleosides and their sequences. Carell et al. have developed heterogeneous arrays of 5–10 metal ions of two different kinds by using combined sequences of salen (**S**)-nucleobases and thymines (**T**) which form ethylenediamine-cross-linked **S**–Cu^{2+}(en)–**S** base pairs and **T**–Hg^{2+}–**T** base pairs [31,32], respectively [34]. Site selective and quantitative arraying of Cu^{2+} and Hg^{2+} ions in the DNAs were drawn in Fig. 13. The strategy could be expanded to many types of metal ions to develop novel meta-metal communications.

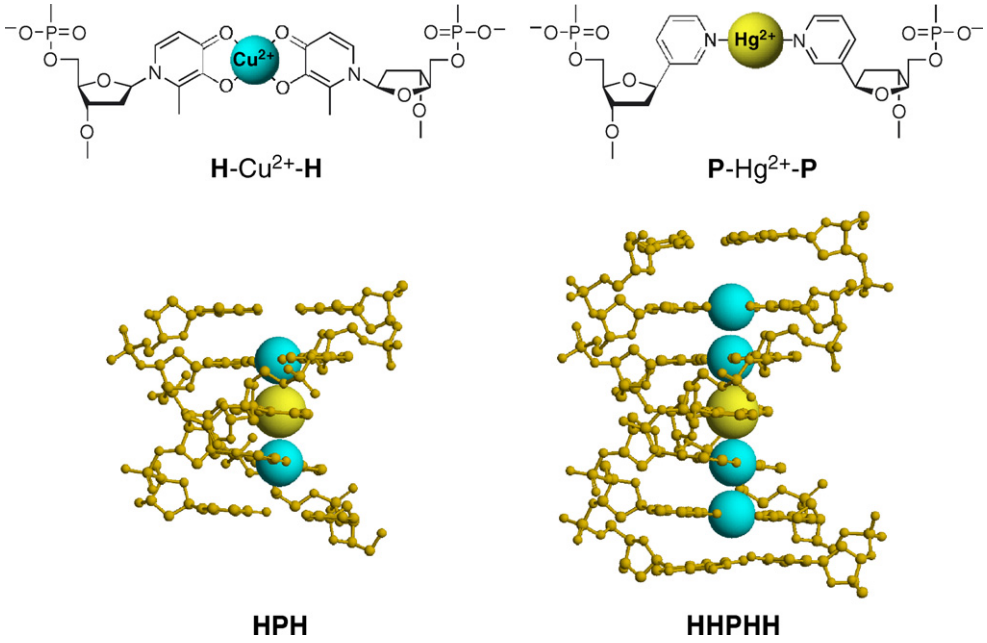


Fig. 12. A plausible structure of Cu^{2+}–Hg^{2+}–Cu^{2+} and Cu^{2+}–Cu^{2+}–Hg^{2+}–Cu^{2+}–Cu^{2+} metal ion arrays in d(5′-G**HPH**C-3′)$_2$ and d(5′-G**HHPHH**C-3′)$_2$, respectively.

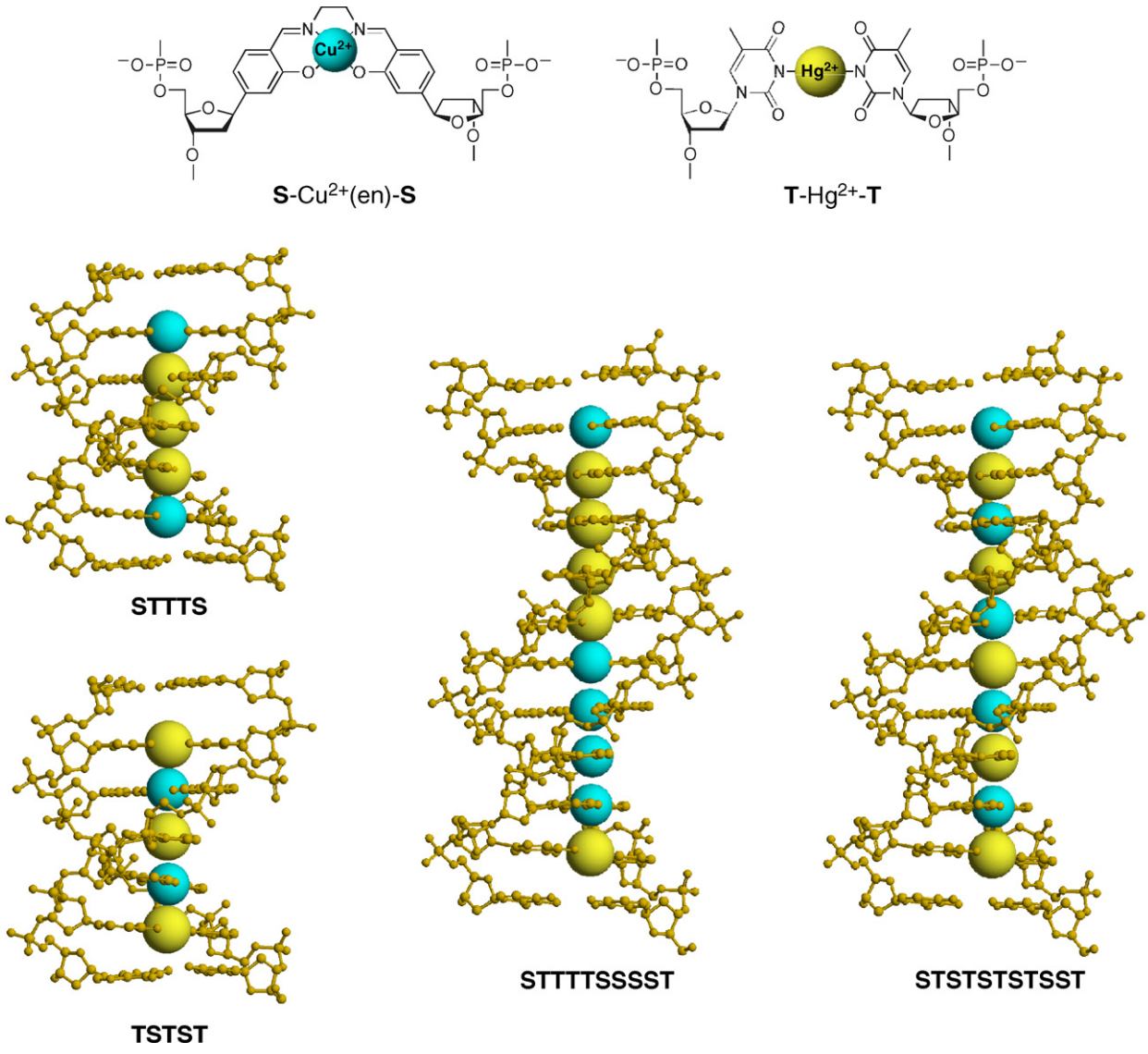


Fig. 13. Variation of metal arrays. Cu^{2+}–Hg^{2+}–Hg^{2+}–Hg^{2+}–Cu^{2+}, Hg^{2+}–Cu^{2+}–Hg^{2+}–Cu^{2+}–Hg^{2+}, Cu^{2+}–Hg^{2+}–Hg^{2+}–Hg^{2+}–Hg^{2+}–Cu^{2+}–Cu^{2+}–Cu^{2+}–Cu^{2+}–Hg^{2+}, and Cu^{2+}–Hg^{2+}–Cu^{2+}–Hg^{2+}–Cu^{2+}–Hg^{2+}–Cu^{2+}–Hg^{2+}–Cu^{2+}–Hg^{2+} metal ion array in $d(NNNNN*****NNNNN)_2$ (N = G or C). Sequences indicated as ***** are **STTTS**, **TSTST**, **STTTTSSSST**, and **STSTSTSTST**, respectively.

6. Conclusions

Precise assembly of metal complexes is becoming increasingly important as a key strategy to develop functional materials, molecular devices and catalysis. The strategies based on structure and the function of DNA are applicable to assembling wide rage of metal complexes, because DNA contains programmable information in a simple and predictable manner. Moreover, chemists can design not only the sequences of nucleobases but also those of nucleotides, inter and intrastrand interactions, and interactions with matrices to give higher information contents. Hence, the potential of DNA-based programmable assembly of functions of metal complexes is quite high.

Towards the next stage of the DNA-based nanotechnology, specific topics we find of particular importance and interest include: (1) extension the strategy to more complex and larger systems without any dispersion, (2) controlling electrical communication between assembled metal complexes, (3) structural and functional switching at the right time, (4) conjugation with other materials on the DNA-templated assembly, and (5) manipulation of the discrete assembled molecular structure. This field is still in its early stage, but will be quickly expanded to broad research fields. We will soon see important applications of this strategy both to material sciences and biotechnologies.

References

[1] J.-M. Lehn, Supramolecular Chemistry. Concepts and Perspectives, VCH, Weinheim, 1995.
[2] N. Kimizuka, in: A. Ciferri (Ed.), Supramolecular Polymers, 2nd ed., CRC Press LLC, Boca Raton, FL, 2005, p. 481.
[3] (a) R. Dobrawa, F. Würthner, J. Polym. Sci. A 43 (2005) 4981;
(b) F. Ciardelli, E. Tsuchida, D. Wohrle (Eds.), Macromolecule-Metal Complexes, Springer, New York, 1996.

[4] (a) R.M. Yeh, A.V. Davis, K.N. Raymond, in: T.J. Meyer (Ed.), Comprehensive Coordination Chemistry II, Elsevier Ltd., Oxford, UK, 2004, p. 327;
(b) M. Fujita, Chem. Soc. Rev. 27 (1998) 417.
[5] (a) E.C. Constable, in: T.J. Meyer (Ed.), Comprehensive Coordination Chemistry II, Elsevier Ltd., Oxford, UK, 2004, p. 263;
(b) S.-Y. Lai, T.-W. Lin, Y.-H. Chen, Wang, G.-H. Lee, M.-H. Yang, M.-K. Leung, S.-M. Peng, J. Am. Chem. Soc. 121 (1999) 250;
(c) T. Murahashi, H. Kurosawa, Coord. Chem. Rev. 231 (2002) 207.
[6] M.J. Gait (Ed.), Oligonucleotide Synthesis: A Practical Approach, IRL Press, New York, 1990.
[7] (a) N.C. Seeman, Nature 421 (2003) 427;
(b) N.C. Seeman, Int. J. Nanotechnol. 2 (2005) 348;
(c) N.C. Seeman, Meth. Mol. Biol. 303 (2005) 143;
(d) N.C. Seeman, P.S. Lukeman, Rep. Prog. Phys. 68 (2005) 237.
[8] (a) C.M. Niemeyer, Appl. Phys. A 68 (1999) 119;
(b) C.M. Niemeyer, Curr. Opin. Chem. Biol. 4 (2000) 609;
(c) C.M. Niemeyer, Angew. Chem. Int. Ed. 40 (2001) 4128;
(d) C.M. Niemeyer, Trends. Biotechnol. 20 (2002) 395.
[9] K.V. Gothelf, T.H. LaBean, Org. Biomol. Chem. 3 (2005) 4023.
[10] J. Wangel, Org. Biomol. Chem. 2 (2004) 277.
[11] J.J. Storhoff, C.A. Mirkin, Chem. Rev. 99 (1999) 1849.
[12] Y. Sun, C.-H. Kiang, in: H.S. Nalwa (Ed.), Handbook of Nanostructured Biomaterials and their Applications in Nanobiotechnology, vol. 2, American Scientific Publishers, Stevenson Ranch, 2005, p. 223.
[13] K. Tanaka, M. Shionoya, Chem. Lett. 35 (2006) 694.
[14] (a) H. Asanuma, T. Ito, T. Yoshida, X.G. Liang, M. Komiyama, Angew. Chem. Int. Ed. 38 (1999) 2393;
(b) H. Kashida, M. Tanaka, S. Baba, T. Sakamoto, G. Kawai, H. Asanuma, M. Komiyama, Chem. Eur. J. 12 (2006) 777;
(c) M.D. Sørensen, M. Petersen, J. Wengel, Chem. Commun. (2003) 2130;
(d) M. Nakamura, Y. Ohtoshi, K. Yamana, Chem. Commun. (2005) 5163.
[15] D.J. Hurley, Y. Tor, J. Am. Chem. Soc. 120 (1998) 2194.
[16] H. Morales-Rojas, E.T. Kool, Org. Lett. 4 (2002) 4377.
[17] (a) J.A. Piccirilli, T. Krauch, S.E. Moroney, S.A. Benner, Nature 343 (1990) 33;
(b) E.T. Kool, Acc. Chem. Res. 35 (2002) 936;
(c) D.L. McMinn, A.K. Ogawa, Y. Wu, J. Liu, P.G. Schultz, F.E. Romesberg, J. Am. Chem. Soc. 121 (1999) 11585.
[18] M. Shionoya, K. Tanaka, Curr. Opin. Chem. Biol. 8 (2004) 592.
[19] K. Tanaka, M. Shionoya, J. Org. Chem. 64 (1999) 5002.
[20] (a) K. Tanaka, M. Tasaka, H. Cao, M. Shionoya, Eur. J. Pharm. Sci. 13 (2001) 77;
(b) H. Cao, K. Tanaka, M. Shionoya, Chem. Pharm. Bull. 48 (2000) 1745.
[21] (a) M. Tasaka, K. Tanaka, M. Shiro, M. Shionoya, Supramol. Chem. 13 (2001) 671;
(b) K. Tanaka, M. Tasaka, H. Cao, M. Shionoya, Supramol. Chem. 14 (2002) 255.
[22] K. Tanaka, Y. Yamada, M. Shionoya, J. Am. Chem. Soc. 124 (2002) 8802.
[23] K. Tanaka, A. Tengeiji, T. Kato, N. Toyama, M. Shiro, M. Shionoya, J. Am. Chem. Soc. 124 (2002) 12494.
[24] M. Shionoya, K. Tanaka, Bull. Chem. Soc. Jpn. 73 (2000) 1945.
[25] (a) E. Meggers, P.L. Holland, W.B. Tolman, F.E. Romesberg, P.G. Schultz, J. Am. Chem. Soc. 122 (2000) 10714;
(b) S. Atwell, E. Meggers, G. Spraggon, P.G. Schultz, J. Am. Chem. Soc. 123 (2001) 12364;
(c) N. Zimmermann, E. Meggers, P.G. Schultz, J. Am. Chem. Soc. 124 (2002) 13684;
(d) N. Zimmermann, E. Meggers, P.G. Schultz, Bioorg. Chem. 32 (2004) 13.
[26] (a) H. Weizman, Y. Tor, Chem. Commun. (2001) 43;
(b) H. Weizman, Y. Tor, J. Am. Chem. Soc. 123 (2001) 3375.
[27] C. Brotschi, C.J. Leumann, Nucleosides, Nucleot. Nucl. Acids 22 (2003) 1195.
[28] (a) C. Switzer, S. Sinha, P.H. Kim, B.D. Heuberger, Angew. Chem. Int. Ed. 44 (2005) 1529;
(b) C. Switzer, D. Shin, Chem. Commun. (2005) 1342.
[29] (a) G.H. Clever, K. Polborn, T. Carell, Angew. Chem. Int. Ed. 44 (2005) 7204;
(b) G.H. Clever, Y. Söltl, H. Burks, W. Spahl, T. Carell, Chem. Eur. J. 12 (2006) 8708;
(c) G.H. Clever, T. Carell, Angew. Chem. Int. Ed. 46 (2007) 250.
[30] J. Mueller, D. Boehme, P. Lax, M.M. Cerda, M. Roitzsch, Chem. Eur. J. 11 (2005) 6246.
[31] Z. Kuklenyik, L.G. Marzilli, Inorg. Chem. 36 (1996) 5654.
[32] (a) A. Ono, F. Togashi, Angew. Chem. Int. Ed. 43 (2004) 2300;
(b) Y. Tanaka, S. Oda, H. Yamaguchi, Y. Kondo, C. Kojima, A. Ono, J. Am. Chem. Soc. 128 (2007) 2172;
(c) Y. Miyake, H. Togashi, M. Tashiro, H. Yamaguchi, S. Oda, M. Kudo, Y. Tanaka, Y. Kondo, R. Sawa, T. Fujimoto, T. Machinami, A. Ono, J. Am. Chem. Soc. 128 (2006) 2172.
[33] K. Tanaka, A. Tengeiji, T. Kato, N. Toyama, M. Shionoya, Science 299 (2003) 1212.
[34] K. Tanaka, G.H. Clever, Y. Takezawa, Y. Yamada, C. Kaul, M. Shionoya, T. Carell, Nature Nanotech. 1 (2006) 190.