DNA Structures

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Metal-Locked DNA Three-Way Junction**

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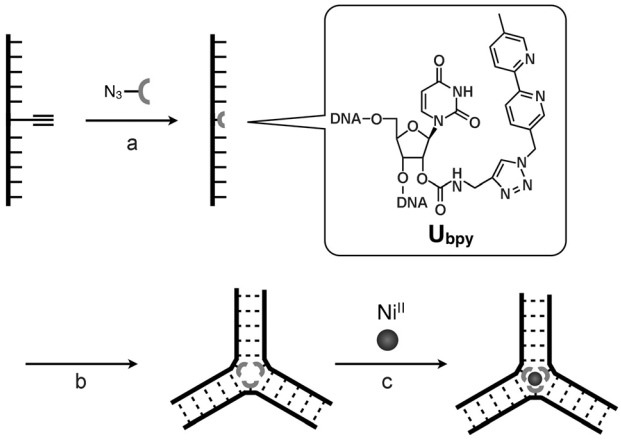
DNA has attracted great interest as a promising component of nanoscale architectures because of its well-ordered structures and highly programmable nature. In particular, the conjugation of natural DNA structures with artificial functional components has opened up a growing field of supramolecular chemistry and DNA nanotechnology, which has endowed DNA with unprecedented hybridization properties and allowed the resulting structures to be controllable with external stimuli.[1,2] A particularly attractive approach to obtain controllable DNA motifs is to incorporate into the DNA scaffolds metal complexes, whose coordination structures as well as thermodynamic and kinetic stabilities can be regulated by the judicious selection of metal ions and careful design of ligand-modified artificial nucleosides.

We have developed metal-mediated base pairs in which natural hydrogen bonds between nucleobases were replaced by metal coordination bonds.[3] The incorporation of the metallo-base pairs into DNA resulted in the stabilization of both duplexes[4] and triplexes,[5] and led to discrete metal assembly inside the structures.[6,7] Furthermore, triple-stranded structures with arrays of hexacoordinate Fe^{III} ions were constructed on the basis of a 3:1 ligand–metal complexation.[8] Other research groups have also constructed DNA–metal conjugates with various DNA structural motifs starting from DNA duplexes,[3,9] triplexes,[10] G-quadruplexes,[11] and single junction motifs[12–14] through to large, vertex-linked interlocked DNA structures.[15,16]

Of the various nucleic acid structures, DNA branching structures are notably essential structural motifs for DNA origami (as a cross-over motif)[17–19] and 3D DNA nanostructures, such as DNA polyhedra (as a vertex motif).[20] Despite its growing importance, metal-mediated stabilization of DNA junction structures has not previously been achieved. Herein, we extend our method of metal-mediated base-pairing to DNA junctions, which could render branched structures more suitable for use in the assembly of nanoscale DNA structures.

We have looked to modify DNA three-way junction structures through the formation of a ligand–metal complex at the junction point.[21] This approach offers an attractive combination of stable yet controllable DNA architectures with novel capabilities. Such systems could act as rigid, functionalizable vertices of 2D and 3D nanostructures, but could also be exploited as chiral reaction spaces. In particular, we envisaged the use of 3:1 ligand–metal complexation with octahedral hexacoordinated metal ions, expecting that this would allow the stoichiometric cross-linking of three strands at the branching point. We chose a bidentate bipyridine (bpy) derivative as the ligand moiety, which has been used successfully to replace hydrogen-bonding nucleobases in both DNA duplexes[22–25] and PNA duplexes.[26,27] The optimal position for incorporation of the ligand was determined to be at the 2′-position of a nucleoside, specifically uridine, which directs the ligands into the center of the junction core (Scheme 1). The attachment of the bpy ligands to DNA was accomplished through a postsynthetic click reaction[28,29] to avoid both a lengthy synthesis and commonly occurring problems, such as low solubility of the intermediates. Additionally, it offers the possibility of forming large libraries of modified oligonucleotides for rapid combinatorial screening.



$\mathbf{L_1}/\mathbf{S_1}$ 5′-GAA GGA ACG **X**AC ACT CGC AG-3′
$\mathbf{L_2}/\mathbf{S_2}$ 5′-GTT CCA CGC **X**AC GTT CCT TC-3′
$\mathbf{L_3}/\mathbf{S_3}$ 5′-CTG CGA GTG **X**AG CGT GGA AC-3′

$\mathbf{L_1}$–$\mathbf{L_3}$: **X** = $\mathbf{U_{bpy}}$, $\mathbf{S_1}$–$\mathbf{S_3}$: **X** = **T**

Scheme 1. Schematic representation of the formation of metal-locked DNA three-way junctions. a) Cu^{I}-catalyzed [3+2] Huisgen cycloaddition of bipyridine azide to three different alkyne-modified DNA oligonucleotides. b) Assembly of modified DNA into a three-way junction structure. c) Stabilization of the junction structure by addition of Ni^{II} ions. The sequences of the bpy-modified DNA strands ($\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_3}$) and those of unmodified control strands ($\mathbf{S_1}$, $\mathbf{S_2}$, and $\mathbf{S_3}$) are shown.

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An artificial nucleoside possessing an alkyne group at the 2′-position[30] was incorporated into the middle of three DNA strands that were previously reported to exclusively form a three-way junction with thymine at the center.[31] The alkyne-modified strands were reacted under Cu^{I}-catalyzed Huisgen cycloaddition conditions with a bipyridine azide, thereby yielding the bpy-modified strands ($\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_3}$, see the Supporting Information). Subsequent hybridization of the three strands afforded the three-way junction structure ($\mathbf{L_1L_2L_3}$) containing a preorganized metal-binding site at its core (Scheme 1).

We first evaluated the stability of the bpy-modified system ($\mathbf{L_1L_2L_3}$) relative to the unmodified DNA three-way junction ($\mathbf{S_1S_2S_3}$) in the presence and absence of various divalent first-row transition metal ions (Figure 1). All the samples were annealed both before and after the addition of metal ions to afford the thermodynamic products. Melting curve analysis showed that the modified DNA junction was highly and selectively stabilized in the presence of low concentrations of divalent metals, whilst the natural junction did not exhibit any stabilization (see Figure S1 in the Supporting Information). Metal ions that can preferentially form tris-bpy octahedral complexes increased the stability of the junction in the order $Ni^{II} > Fe^{II} > Co^{II}$, which concurs with the order of the β_3 values of $[M(bpy)_3]^{2+}$ complexes ($\log\beta_3 = 20.2$, 17.2, and 15.9 for Ni^{II}, Fe^{II}, and Co^{II} ions, respectively).[32] In contrast, weaker binding metals such as Mn^{II} and Zn^{II} ($\log\beta_3 = 5.6$ and 13.2, respectively) and those with a preference for non-octahedral binding, such as Cu^{II}, showed little stabilization upon addition to the system.

The results (Table 1; see Table S1 in the Supporting Information for other metal ions) show that Ni^{II} ions have the greatest stabilization effect, increasing the thermal denaturation temperature (T_m) of the three-way junction ($\mathbf{L_1L_2L_3}$) by 9 °C compared to the metal-free junction, and by over 12 °C compared to the unmodified junction ($\mathbf{S_1S_2S_3}$). Similar metal-dependent stabilization has also been observed with bpy-modified DNA duplexes[23,25] and PNA duplexes.[27] In contrast, modification of the corresponding duplex form ($\mathbf{L_1L_4}$) with bpy resulted in significant destabilization, both in the absence ($\Delta T_m^{bpy} = -15.0$ °C) and the presence of Ni^{II} ions ($\Delta T_m^{bpy} = -6.5$ °C), compared to the unmodified $\mathbf{S_1S_4}$ duplex (see Figure S4 in the Supporting Information). This result justifies our design strategy based on the idea that 3:1 ligand–metal complexation can efficiently and selectively stabilize three-way junction structures.

The stabilization effect was further evaluated by varying the ratio of Ni^{II} ions to the bpy-modified three-way junction ($\mathbf{L_1L_2L_3}$). The melting profiles showed that the stability of the system was enhanced with an increasing concentration of the metal ion up to one equivalent (i.e., $[Ni^{II}]/[\mathbf{L_1L_2L_3}] = 1.0{:}1$). Excess Ni^{II} ions resulted in a decrease in the stabilization (Figure 2). Accordingly, the addition of one equivalent of Ni^{II} ions appears to be sufficient to stabilize the three-way junction and illustrates the strength and selectivity of the bpy-modified DNA–metal interaction. The stoichiometry observed here clearly suggests that 3:1 ligand–metal complexation, in other words formation of the $[Ni(bpy)_3]^{2+}$ complex, brought about the stabilization of the three-way junction.

Table 1: Melting temperatures (T_m) of unmodified ($\mathbf{S_1S_2S_3}$) and bpy-modified three-way junctions ($\mathbf{L_1L_2L_3}$) with and without one equivalent of first-row transition-metal ions (M^{II}).[a]

	$\mathbf{S_1S_2S_3}$		$\mathbf{L_1L_2L_3}$		
Metal ion	none	none	Fe^{II}	Co^{II}	Ni^{II}
T_m [°C][b]	46.2	49.9	54.9[c]	53.2	58.8
ΔT_m^{bpy} [°C][d]	–	+3.7	+8.7	+7.0	+12.6
ΔT_m^{M} [°C][e]	–	–	+5.0	+3.3	+8.9

[a] Average of at least 3 runs after annealing. [b] The T_m value was calculated as the temperature at which the change in the absorbance at 260 nm (ΔA_{260}) was 50%. [c] Average value of 3 non-annealed runs because of oxidation of the metal species. The stabilization decreased on subsequent runs. [d] ΔT_m^{bpy} represents the difference in the T_m value relative to that of the unmodified three-way junction ($\mathbf{S_1S_2S_3}$). [e] ΔT_m^{M} represents the difference in the T_m value relative to that of the metal-free three-way junction ($\mathbf{L_1L_2L_3}$).

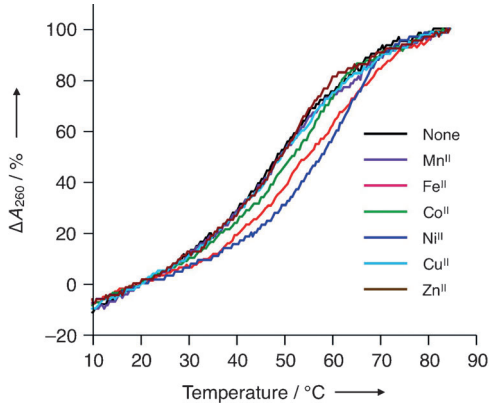

Figure 1. Melting curves of the bpy-modified DNA three-way junction ($\mathbf{L_1L_2L_3}$) in the presence of different M^{II} ions. $[\mathbf{L_1L_2L_3}] = 1.0$ μM, $[M^{II}] = 0$ and 1.0 μM in 10 mM 3-(*N*-morpholine)propanesulfonic acid (MOPS) buffer (pH 7.0), 100 mM NaCl, 0.2 °C min^{-1}, $\Delta A_{260} = \{A_{260}(t\,°C) - A_{260}(20\,°C)\}/\{A_{260}(85\,°C) - A_{260}(20\,°C)\} \times 100$.

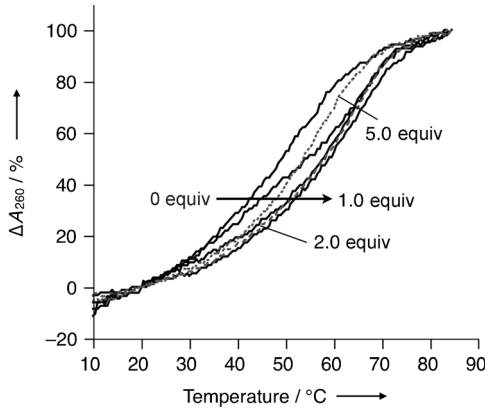

Figure 2. Melting curves of the bpy-modified DNA three-way junction ($\mathbf{L_1L_2L_3}$) in the presence of different concentrations of Ni^{II} ions. $[\mathbf{L_1L_2L_3}] = 1.0$ μM, $[Ni^{II}] = 0$, 0.3, 0.7, 1.0 (——), 2.0 (- - - - -), and 5.0 μM (•••••) in 10 mM MOPS buffer (pH 7.0), 100 mM NaCl, 0.2 °C min^{-1}, $\Delta A_{260} = \{A_{260}(t\,°C) - A_{260}(20\,°C)\}/\{A_{260}(85\,°C) - A_{260}(20\,°C)\} \times 100$.

Furthermore, the melting curves recorded in the presence of less than one equivalent of Ni^{II} ions show an apparent two-step transition, which might indicate the presence of two different species, namely, a less-stable metal-free three-way junction and a more stable one in which a $[Ni(bpy)_3]^{2+}$ complex was formed. This demonstrates a cooperative coordination as a result of the preorganization of three bpy ligands at the junction core.

The melting profiles of three-way junctions possessing a different number of bpy ligands were also studied to confirm the stoichiometry of the Ni^{II} binding (Figure 3). Unlike the

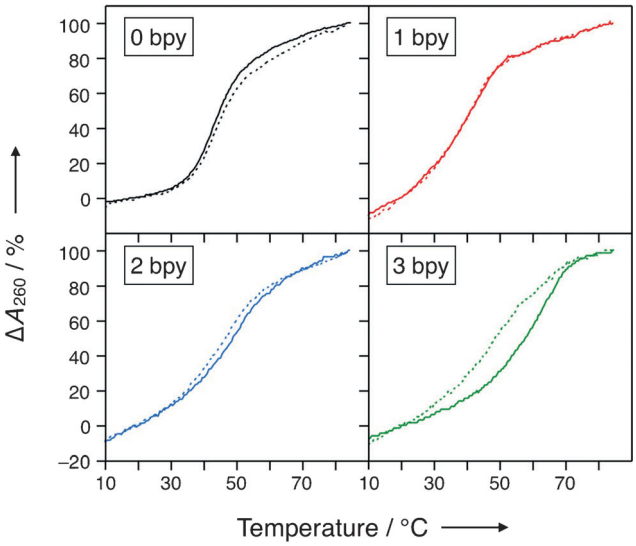

Figure 3. Melting curves of DNA three-way junctions modified with different numbers of bipyridine units in the absence (-----) and presence (——) of Ni^{II} ions. 0 bpy: $\mathbf{S_1S_2S_3}$, 1 bpy: $\mathbf{S_1S_2L_3}$, 2 bpy: $\mathbf{S_1L_2L_3}$, 3 bpy: $\mathbf{L_1L_2L_3}$. [three-way junction] = 1.0 μM, $[Ni^{II}]$ = 0 and 1.0 μM in 10 mM MOPS buffer (pH 7.0), 100 mM NaCl, 0.2 °C min^{-1}, $\Delta A_{260} = \{A_{260}(t\,°C) - A_{260}(20\,°C)\}/\{A_{260}(85\,°C) - A_{260}(20\,°C)\} \times 100$.

triply modified junction (3 bpy, $\mathbf{L_1L_2L_3}$), neither a singly modified (1 bpy, $\mathbf{S_1S_2L_3}$) nor a doubly modified (2 bpy, $\mathbf{S_1L_2L_3}$) junction was stabilized by the addition of one equivalent of Ni^{II} ions. Full stabilization is only achieved in the presence of three bpy units with one equivalent of Ni^{II} ions. Taken together, the stabilization is attributed to cross-linking between three strands through the formation of a $[Ni(bpy)_3]^{2+}$ complex.

The binding of a Ni^{II} ion to the bpy moieties is evident from the UV spectrum (Figure 4). A new absorption band appeared in a linear fashion around 318 nm upon addition of up to one equivalent of Ni^{II} ions. This band is ascribable to the π-π* transition of the coordinated bpy ligands of the $[Ni(bpy)_3]^{2+}$ complex.[33] An increase in the absorbance was still observed beyond one equivalent, but the rate of change in the intensity was different to that below one equivalent. Considering the fact that the addition of more than one equivalent of Ni^{II} ions did not enhance the junction stability, the increase in the UV absorbance beyond one equivalent may represent the formation of nonstabilizing Ni^{II}–ligand species, perhaps with coordination to triazole rings or neighboring nucleobases.

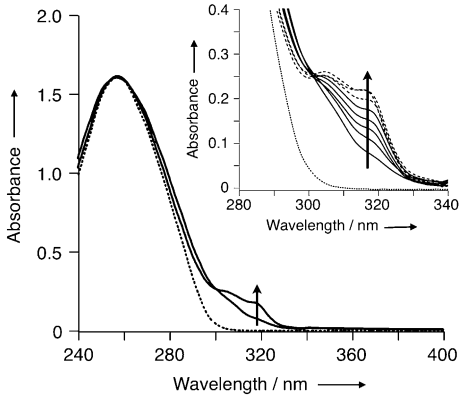

Figure 4. UV spectra of the unmodified DNA three-way junction ($\mathbf{S_1S_2S_3}$, -----) and the bpy-modified three-way junction ($\mathbf{L_1L_2L_3}$, ——) in the absence and the presence of Ni^{II} ions. [$\mathbf{L_1L_2L_3}$] or [$\mathbf{S_1S_2S_3}$] = 2.5 μM, $[Ni^{II}]$ = 0 and 2.5 μM in 10 mM MOPS buffer (pH 7.0), 100 mM NaCl, l = 1.0 cm, 20 °C. Inset: $[Ni^{II}]$ = 0, 0.75, 1.25, 1.75, 2.5 (——), 3.75, 5.0, and 12.5 μM (-----).

To determine the structure of the $[Ni(bpy)_3]^{2+}$ complex at the heart of the junction, we attempted to model the system. The predicted structure shows that the complex sits just above the core of the junction and must adopt a *fac* configuration for the strands to correctly assemble (Figure 5). However, the

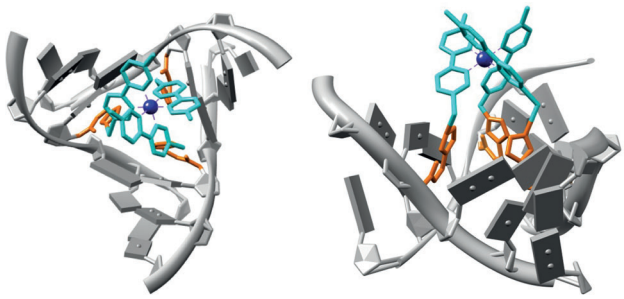

Figure 5. Proposed structure of the preferred Λ-*fac*-$[Ni(bpy)_3]^{2+}$ complex at the junction core. Gray: DNA three-way junction scaffold, blue: $[Ni(bpy)_3]^{2+}$ complex, orange: triazole linkage.

modeling studies showed no clear preference for the Δ or Λ configuration of the metal complex, each being theoretically capable of forming.

The circular dichroism (CD) spectra were measured to further elucidate the structure of the Ni^{II}-conjugated three-way junction (Figure 6). The spectrum of the metal-free junction ($\mathbf{L_1L_2L_3}$) showed a large signal around 260 nm, thus indicating a typical B-DNA conformation of the duplex region, as well as a shoulder band from the bpy units reaching to 340 nm, which suggests a degree of preorganization of the three bpy ligands at the junction point. Interestingly, the addition of one equivalent of Ni^{II} ions results in a strong positive Cotton effect, with a maximum at approximately 320 nm, and a significant decrease in the CD intensity around 300 nm. This is believed to arise from exciton coupling of the long-axis polarized transitions of the three bpy ligands in the $[Ni(bpy)_3]^{2+}$ complex,[34] further confirming the formation of

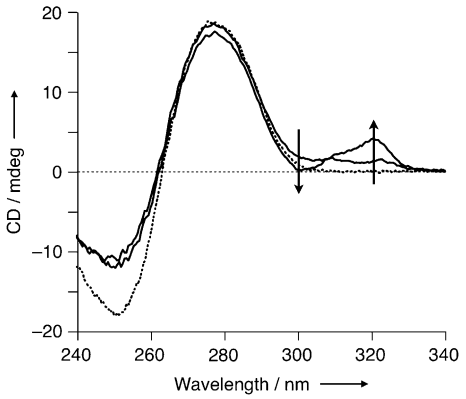

Figure 6. CD spectra of the unmodified DNA three-way junction (**$S_1S_2S_3$**, -----) and the bpy-modified three-way junction (**$L_1L_2L_3$**, ——) in the absence and presence of Ni^{II} ions. [**$L_1L_2L_3$**] or [**$S_1S_2S_3$**] = 2.5 μM, [Ni^{II}] = 0 and 2.5 μM in 10 mM MOPS buffer (pH 7.0), 100 mM NaCl, l = 1.0 cm, 20 °C.

a metal complex. The signage of the observed Cotton effect is consistent with related octahedral Λ-$[Ni(bpy)_3]^{2+}$ isomers,[34,35] and is thus indicative of the predominant formation of the Λ isomer at the junction core, as depicted in Figure 5.[36] The CD signal is expected to arise from a transfer of chirality from the DNA to the metal complex as a result of preorganization of the bpy ligands at the junction core.[35,37] Of particular note is the fact that the diastereoselectivity was not lost over time, with the Cotton bands being unchanged after four days at room temperature. This finding indicates that the Ni^{II} complex at the DNA three-way junction is stable and resistant to racemization; in contrast, the free $[Ni(bpy)_3]^{2+}$ complex is rapidly racemized in aqueous solution.[38]

In this study, we synthesized a DNA three-way junction structure modified with preorganized bpy ligands which can be specifically and uniquely stabilized by the addition of one equivalent of Ni^{II} ions by forming a $[Ni(bpy)_3]^{2+}$ complex at the junction core. This simple molecular design concept has firmly established that a 3:1 ligand–metal complexation stabilizes junction structures consisting of three strands. Such a concept could be easily further applied to other branching structures, such as four-way junctions. Although metal selectivity and detailed coordination structure are still difficult to predict, we envisage that the metal-locked junction system presented here will significantly increase the programmability of DNA nanostructures. The metal complex formed showed a diastereomeric preference that could be a result of the chiral DNA environment at the core of the junction. Consequently, this system may also be utilized in the area of DNA-based chirality induction and asymmetric catalytic reactions.

This structural motif can be embedded into DNA origami and 3D DNA nanoarchitectures, thus providing a wide variety of DNA structures whose stability and rigidity can be regulated by reversible metal coordination at the branching points. Therefore, the metal-locked DNA junction shows promise as a potential component of metal-triggered (for example, redox-responsive or pH-sensitive) DNA nanomachines and DNA nanodevices, which should be among the next and most challenging targets in the field of DNA nanotechnology.

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