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COMMUNICATION

Light-induced formation of thymine-containing mercury(II)-mediated base pairs

Shuvankar Naskar[a] and Jens Müller*[a]

Abstract: By applying caged thymidine residues, DNA duplexes were created in which Hg^{II}-mediated base pair formation can be triggered by irradiation with light. When a bidentate ligand was used as the complementary nucleobase, an unprecedented stepwise formation of different metal-mediated base pairs was achieved.

Metal-mediated base pairs represent a prominent type of nucleic acid functionalization. By using ligand-containing nucleosides, hydrogen bonds within a base pair can formally be replaced by a centrally located metal ion.[1] The T–Hg^{II}–T (Fig. 1a) and C–Ag^{I}–C base pairs involving the canonical thymine (T) and cytosine (C) residues are among the best investigated metal-mediated base pairs.[1c] In addition, numerous artificial nucleobases have been shown to be useful in the generation of metal-mediated base pairs designed for particular functionalities.[2] In several cases, crystal structures and solution structures have confirmed the proposed base pairing patterns.[3] As a result of the additional metal-based functionality, metal-mediated base pairs have been applied in a variety of research areas, ranging from DNA charge transfer[4] and oligonucleotide sensors[5] to the generation of DNA-templated metal clusters[6] and switchable devices.[7] Whenever a switching functionality has been introduced in the context of metal-mediated base pairing, the switching process (mostly of DNA topology) was triggered by the addition (or removal) of a suitable metal ion. In this communication, we report for the first time the light-triggered formation of a metal-mediated base pair. Several examples exist for the use of light to regulate DNA function.[8] Many of these involve the application of so-called caged nucleobases, i.e. nucleobases carrying a photo-removable protecting group.[9] Thymine has been one of the first nucleobases investigated in the context of photo-caged nucleobases.[10]

As thymine is well-known to coordinate to Hg^{II} ions, we decided to probe the light-triggered Hg^{II}-mediated base pair formation of caged thymidine. Towards this end, a caged thymidine derivative T_{NPP} with well-established caging properties (Fig. 1b)[10] was introduced into different oligonucleotide sequences (Table 1). The duplex sequence applied in this study has previously been used in many reports on metal-mediated base pairs, allowing a comparison with other metal-mediated base pairs.[11] Duplexes **I** – **IV** bear one central T:T mismatch, with the caged nucleobase being located either in the pyrimidine-rich strand (duplex **I**), in the purine-rich strand (duplex **II**) or in both strands (duplex **III**). Duplex **IV** with unprotected thymine residues serves as a reference. Similarly, duplexes **V** – **VII** contain one central T:P base pair. The artificial phenanthroline-derived nucleoside analogue P has previously been shown to form a stable Hg^{II}-mediated base pair with thymine, but not with cytosine.[2k] While the central thymine residue in duplex **V** bears a photo-cleavable protecting group, duplexes **VI** and **VII** serve as references bearing an unprotected thymidine (duplex **VI**) or a non-cleavable substituent (duplex **VII**).

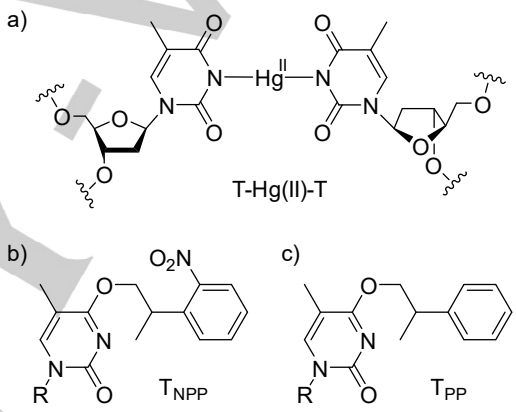

Figure 1. Schematic representation of a) metal-mediated T–Hg^{II}–T base pair, b) thymine residue T_{NPP} bearing a photo-removable protecting group, c) thymine residue T_{PP} bearing a similar protecting group that is not removed upon irradiation.

Table 1. DNA duplexes under investigation in the present study.[a]

Duplex		Sequence
I	ODN1	5'-d(CTT TCT T_{NPP}TC CCT C)
	ODN2	3'-d(GAA AGA TAG GGA G)
II	ODN3	5'-d(CTT TCT TTC CCT C)
	ODN4	3'-d(GAA AGA T_{NPP}AG GGA G)
III	ODN1	5'-d(CTT TCT T_{NPP}TC CCT C)
	ODN4	3'-d(GAA AGA T_{NPP}AG GGA G)
IV	ODN3	5'-d(CTT TCT TTC CCT C)
	ODN2	3'-d(GAA AGA TAG GGA G)
V	ODN1	5'-d(CTT TCT T_{NPP}TC CCT C)
	ODN5	3'-d(GAA AGA PAG GGA G)
VI	ODN3	5'-d(CTT TCT TTC CCT C)
	ODN5	3'-d(GAA AGA PAG GGA G)
VII	ODN6	5'-d(CTT TCT T_{PP}TC CCT C)
	ODN5	3'-d(GAA AGA PAG GGA G)

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[a] T_{NPP} = thymidine bearing a (2-nitrophenyl)propoxy group, T_{PP} = thymidine bearing a phenylpropoxy group, P = (*S*)-3-(1*H*-Imidazo[4,5-*f*][1,10]-phenanthrolin-1-yl)propane-1,2-diol.

The formation of coordinate bonds in a metal-mediated base pair is typically accompanied by an increase in the DNA duplex melting temperature T_m.[12] Accordingly, metal-mediated base pair formation was probed by temperature-dependent UV spectroscopy. Towards this end, the melting temperature of each duplex was determined in the absence of Hg^{II}, after the addition of one equivalent of Hg^{II} prior to irradiation, in the presence of one equivalent of Hg^{II} after irradiation, and in the presence of two equivalents (i.e. excess) of Hg^{II} after irradiation. Table 2 lists the melting temperatures as derived from the temperature-dependent UV spectra. Fig. 2 exemplifies the melting curves of duplex **I** at pH 6.8.

Table 2. Melting temperatures T_m of the DNA duplexes.[a]

Duplex	pH	T_m / °C	T_m / °C	T_m / °C	ΔT_m / °C
		0 Hg^{II}, no light	1 Hg^{II}, no light	1 Hg^{II}, irradiated	upon irradiation
I	6.8	29.4(2)	29.3(3)	46.2(4)	+16.9(5)
I	9.0	29.5(5)	28.8(5)	43.4(3)	+14.6(6)
II	6.8	32.1(4)	31.6(4)	45.7(8)	+14.1(9)
II	9.0	30.6(4)	28.6(6)	42.0(6)	+13.4(8)
III	6.8	32.8(6)	32.5(5)	43.8(6)	+11.3(8)[b]
III	9.0	29.9(6)	28.7(5)	39.6(8)	+10.9(9)
IV	6.8	35.5(2)	45.7(2)	45.8(3)	n.a.[c]
IV	9.0	32.4(2)	42.0(2)	41.9(2)	n.a.[c]
V	6.8	34.1(5)	42.0(6)	49.6(9)	+8(1)
VI	6.8	31.7(3)	48.2(4)	48.1(3)	n.a.[c]
VII	6.8	35.5(3)	40.8(8)	40(2)	±0(2)

[a] Given in parenthesis is the standard error (3σ) obtained upon fitting the derivative of the melting curve with a Gauss function (T_m) or using error propagation (ΔT_m). [b] Data for higher melting point of biphasic transition due to incomplete formation of the Hg^{II}-mediated base pair. [c] not applicable.

As can be seen, the addition of Hg^{II} does not lead to any change in T_m prior to irradiation of the sample. After 1 min of irradiation of a heated sample, a significant increase in T_m of ~17 °C is observed. Initial experiments with irradiation at room temperature had resulted in a biphasic melting behavior (Fig. S1a), with the first melting transition coinciding with the T_m of the Hg^{II}-free duplex, suggesting an incomplete photo-deprotection and hence an incomplete formation of the T–Hg^{II}–T pair. Several subsequent attempts to achieve a complete formation of the metal-mediated base pair failed, including an extended irradiation time, the use of a different buffer, and the addition of Hg^{II} after the irradiation rather than prior to it (data not shown). Finally, two conditions were established that lead to a complete T–Hg^{II}–T formation, namely performing the irradiation at elevated temperature (ca. 50 °C) or investigating the duplex at pH 9.0 rather than pH 6.8 (Fig. S1b). The latter is nicely explained by previous mechanistic studies indicating a deprotonation step during photo-deprotection.[13] The photo-deprotection of the oligonucleotides was confirmed mass spectrometrically, as shown exemplarily for ODN1 (Fig. S2). According to the mass spectrum, a minor amount of ODN1 remains protected even under optimized conditions. It is not clear whether this can be attributed to the absence of buffer under the conditions of mass spectrometry. If it is also present in buffer, then this amount is small enough not to be detected in the DNA melting studies.

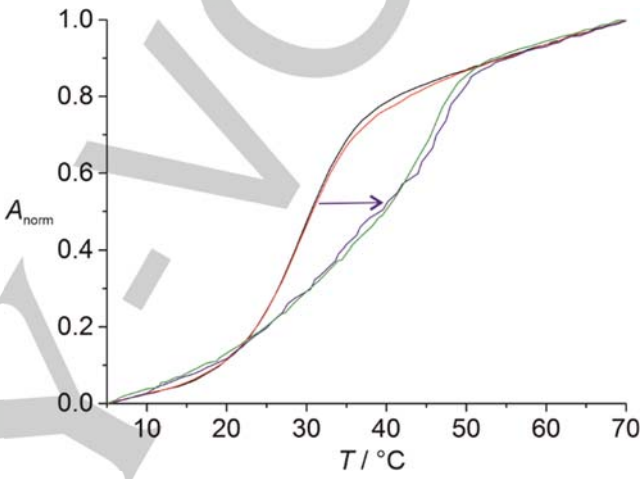

Figure 2. Melting curves of duplex **I** at pH 6.8 in the absence of Hg^{II} (black), in the presence of one equivalent of Hg^{II} prior to irradiation (red), in the presence of one equivalent of Hg^{II} after irradiation (blue) and in the presence of two equivalents of Hg^{II} after irradiation (green). Experimental conditions: 1 μM duplex, 150 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MOPS buffer (pH 6.8).

Essentially the same behavior is found for duplex **II** (Fig. S3), where the T_{NPP}:T pair is formally replaced by a T:T_{NPP} pair. This indicates that the relative position of the caged nucleobase does not significantly influence the outcome of the Hg^{II}-mediated base pair formation. Interestingly, in duplex **III** bearing a T_{NPP}:T_{NPP} pair, the photo-deprotection is incomplete even when heating the sample (Fig. S4a) or when irradiating for an extended time, indicating the relevance of steric factors during deprotection, too. This is confirmed by a mass spectrometric study (Fig. S5), which shows a reduced efficiency of photo-deprotection of ODN1 when present in duplex **III**.[14] Nonetheless, a complete T–Hg^{II}–T formation in duplex **III** is achieved at pH 9.0 (Fig. S4b). An investigation of reference duplex **IV** bearing a central T:T mispair shows the anticipated T–Hg^{II}–T base pair formation immediately after the addition of one equivalent of Hg^{II} (Fig. S6). Here, an irradiation of the solution is not required. In fact, irradiation does not significantly influence T_m any further. For duplexes **I** – **IV**, the formation of the T–Hg^{II}–T pair is accompanied by a decrease in molar ellipticity $[\theta]$ at ~280 nm (Fig. S7). In all four cases, the drop in $[\theta]$ occurs under those conditions that evoke an increase in T_m, confirming a simultaneous deprotection and base pair formation. As can be seen from Table 2, T_m of duplexes **I** – **III** in the absence of Hg^{II} are decreased by 3 – 6 °C with respect to that of duplex **IV**,

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indicating a destabilizing effect of the bulky protecting group. After formation of the T–Hg^{II}–T pair, the melting temperatures of duplexes **I** and **II** are, within standard error, identical to that of duplex **IV**. The melting temperature of duplex **III** is marginally lower, which may indicate the presence of a minor fraction of still protected oligonucleotide even under the optimized photo-deprotection conditions in this case.

In a T–Hg^{II}–T pair, the Hg^{II} ion binds both nucleobases in a monodentate fashion (Fig. 1a). Hence, the Hg–N bond involving the first thymine residue must be formed prior to the formation of the N–Hg bond to the other thymine.[15] A different scenario is anticipated for the T–Hg^{II}–P pair (Fig. 3).[2k] It contains the phenanthroline-derived nucleoside analogue P that had been applied in a series of studies, including the concomitant site-specific incorporation of Ag^{I} and Hg^{II} into the same duplex and the first enantiospecific formation of a metal-mediated base pair.[2k, 16] As P is a bidentate ligand, it is expected to be metalated first during the formation of a metal-mediated base pair,[5b] irrespective of the identity of the complementary nucleobase. If the complementary nucleobase is a thymine residue, then a T–Hg^{II}–P base pair is formed.[2k] The question arises what will happen if the protected T_{NPP} acts as complementary nucleobase. Here, two scenarios are feasible. The steric clash of the metalated P residue and the bulky thymine derivative may result in an extrusion of one base from the duplex,[5b] so that a destabilization of the duplex would be expected. Alternatively, the formation of a Hg^{II}-mediated base pair involving the T_{NPP} ligand may occur, which should be accompanied by a minor duplex stabilization. To evaluate these possibilities, duplex **V** with a central T_{NPP}:P pair was investigated.

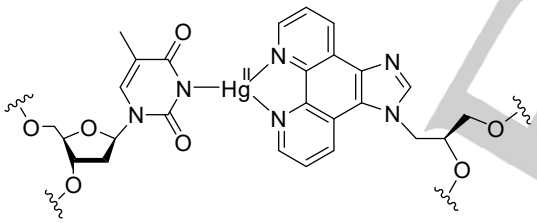

Figure 3. Proposed structure of the metal-mediated T–Hg^{II}–P base pair.

Again, temperature-dependent UV spectroscopy was applied to probe metal-mediated base pair formation. Fig. 4 shows the melting curves obtained for duplex **V**. An increase in T_m of 7.9 ± 0.8 °C is observed after the addition of one Hg^{II} per duplex prior to photo-deprotection, suggesting that a T_{NPP}–Hg^{II}–P base pair is indeed formed with the caged nucleobase. Subsequent irradiation at room temperature leads to a further increase in T_m of 8 ± 1 °C, indicating photo-deprotection and formation of a T–Hg^{II}–P pair. Hence, the chelating phenanthroline-derived ligand P binds the Hg^{II} ion irrespective of the identity of the complementary nucleobase. Even though the thymine residue bears a bulky protecting group, it is forced to engage in metal-mediated base pairing. Metal-mediated base pair formation may additionally be facilitated by the more flexible acyclic backbone of P. Finally, photo-deprotection relieves the steric strain, accompanied by a further increase in the melting temperature.

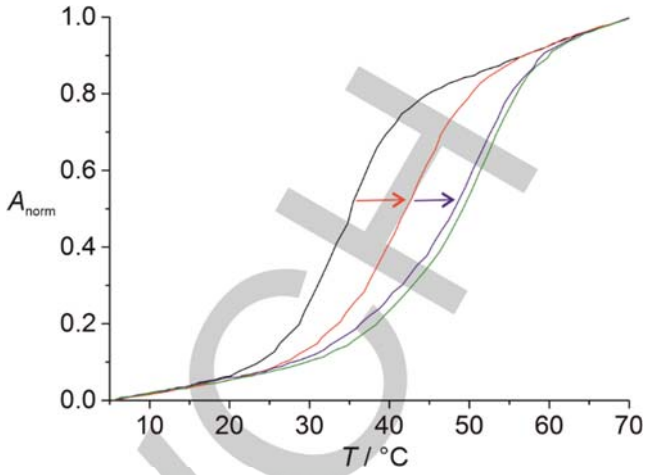

Figure 4. Melting curves of duplex **V** at pH 6.8 in the absence of Hg^{II} (black), in the presence of one equivalent of Hg^{II} prior to irradiation (red), in the presence of one equivalent of Hg^{II} after irradiation (blue) and in the presence of two equivalents of Hg^{II} after irradiation (green). Experimental conditions: 1 μM duplex, 150 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MOPS buffer (pH 6.8).

To confirm this assumption, duplexes **VI** and **VII** bearing a T:P or a T_{PP}:P pair, respectively, were investigated. Duplex **VI** is stabilized by 16.5 ± 0.5 °C upon formation of the T–Hg^{II}–P pair (Fig. S8a). This stabilization is identical to the one observed for duplex **V** upon metal binding and photo-deprotection (16 ± 1 °C). The T_{PP} nucleobase in duplex **VII** bears a substituent of similar size as T_{NPP}. However, this substituent cannot be removed by irradiation. For duplex **VII**, T_m increases by 5.3 ± 0.9 °C upon the addition of Hg^{II} (Fig. S8b). Even though this increase is a bit smaller than that observed for duplex **V** (7.9 ± 0.8 °C), the experiment clearly confirms the applicability of a caged nucleobase in Hg^{II}-mediated base pairing. As anticipated, subsequent irradiation does not lead to a change in T_m. Again, the formation of the metal-mediated base pair can be confirmed CD-spectroscopically. The binding of Hg^{II} to form a T_{NPP}–Hg^{II}–P pair in duplex **V** evokes an increase in $[\theta]$ at ~275 nm (Fig. S9a). The same observation is made for reference duplex **VII** upon the formation of the T_{PP}–Hg^{II}–P pair (Fig. S9c). Generation of the final T–Hg^{II}–P pair in duplex **V** upon photo-deprotection is accompanied by a blue-shift of the positive Cotton effect and a decrease in $[\theta]$ at ~245 nm (Fig. S9a). Again, the same effects are observed upon the formation of the T–Hg^{II}–P pair in reference duplex **VI** (Fig. S9b). Taken together, these data prove that caged nucleobases can be involved in metal-mediated base pairing, provided that the complementary nucleobase is a bidentate ligand. It is interesting to note that the O4-protected thymine residue does not require deprotonation at its N3 position to engage in metal-mediated base pairing, due to its enol tautomeric form (Fig. 1b). In this respect, it appears to resemble cytosine, a nucleobase that is known *not* to form Hg^{II}-mediated base pairs. The formation of a stable $T_{(N)PP}$–Hg^{II}–P pair thus indicates that a simple protonation / deprotonation event cannot explain the preferential binding of Hg^{II} to thymine rather than cytosine and that additional (e.g. electronic) factors must exist, too.

To conclude, we have shown for the first time the light-triggered formation of a metal-mediated base pair, achieved by applying a

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caged thymidine residue. When using a bidentate ligand as the complementary nucleobase, an unprecedented stepwise duplex stabilization was accomplished. Here, the addition of Hg^{II} leads to the formation of a stabilizing metal-mediated base pair involving the caged nucleobase. Subsequent photo-deprotection results in an additional increase in stability. The possibility of using light as an external trigger for metal-mediated base pair formation and the ability to use two orthogonal triggers for the stepwise formation of metal-mediated base pairs of different stability significantly expands the scope of metal-modified nucleic acids. In combination with DNA that switches its topology upon metal-mediated base pair formation, interesting applications are anticipated.

Experimental Section

The phosphoramidites of T_{NPP} and P were prepared according to published procedures.[10b, 17] The T_{PP} nucleoside was prepared in analogy to T_{NPP}.[10b] Details are given in the Supporting Information. All other phosphoramidites were purchased (Glen Research). The oligonucleotides were synthesized and purified as described previously.[17] The desalted oligonucleotides were characterized by MALDI-TOF mass spectrometry (ODN1: calcd. for $[M+H]^+$: 3966 Da, found: 3967 Da; ODN2: calcd. for $[M+H]^+$: 4097 Da, found: 4096 Da; ODN3: calcd. for $[M+H]^+$: 3803 Da, found: 3803 Da; ODN4: calcd. for $[M+H]^+$: 4260 Da, found: 4262 Da; ODN5: calcd. for $[M+H]^+$: 4149 Da, found: 4150 Da; ODN6: calcd. for $[M+H]^+$: 3921 Da, found: 3920 Da). During oligonucleotide quantification, the following molar extinction coefficients were used: T_{NPP}, ε_{260} = 7.5 cm^2 μmol^{-1};[10b] T_{PP}, ε_{260} = 4.2 cm^2 μmol^{-1}; P, ε_{260} = 10.0 cm^2 μmol^{-1}.[5b]

The UV melting experiments were carried out on a UV spectrometer CARY 100 Bio (Agilent) in a 1 cm quartz cuvette. The UV melting profiles were measured in buffer (1 μM DNA duplex, 150 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM buffer (pH 6.8: MOPS, pH 9.0: borate) either with or without $Hg(ClO_4)_2$ at a scan rate of 1 °C min^{-1} with detection at 260 nm. CD spectra were measured using a J-815 spectropolarimeter (JASCO) at 10 °C in the same solution. Each irradiation experiment was performed for 1 min (at ca. 50 °C for duplexes **I** – **III** at pH 6.8 or at room temperature in all other cases) using a 500 W Hg/Xe arc lamp (Newport) equipped with a 1.5 inch water filter and a 335 nm longpass filter (Schott). NMR spectra were recorded on Bruker Avance(I) 400 and Avance(III) 400 instruments. NMR spectra were referenced to residual solvent peaks (CD_3OD, CD_2Cl_2) or to tetramethylsilane ($CDCl_3$).

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Keywords: bioinorganic chemistry • nucleic acid • metal-mediated base pair • caged nucleoside

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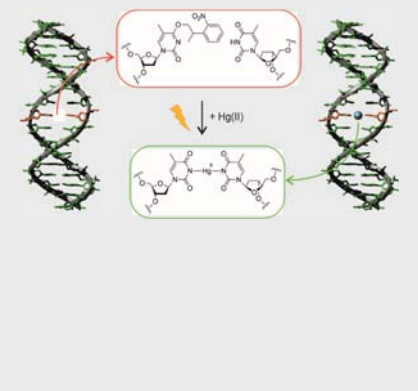
COMMUNICATION

The light-triggered formation of two types of Hg^{II}-mediated base pairs is reported.



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Page No. – Page No.

Light-induced formation of thymine-containing mercury(II)-mediated base pairs

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