Electronic supplementary information

Photoreversible DNA end capping for the formation of hairpin structures

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**Scheme S1.** Photochemical 5’-end capping of ODNs with $^{\text{CNVK}}$.

\[
\begin{align*}
5'\text{A}^{\text{CNVK}}\text{KCGTG} & \quad 3' & 366 \text{ nm, } 0 \degree \text{C} & \quad 3'\text{A}^{\text{CNVK}}\text{KCGTG} \\
3'\text{T}---\text{ACGCAC} & \quad 5' & \quad 5'\text{T}---\text{ACGCAC}
\end{align*}
\]

**Figure S1.** HPLC analysis of the irradiated ODN 1 in the presence of ODN 2. 2’-Deoxyuridine (dU) was used as an internal standard.
Scheme S2. Photochemical 5’-end capping of ODNs with $^{CNVK}$.

\[
\begin{align*}
\text{ODN 3} & \\
5’ & \overset{CNVK}{\text{GCGTG}} & 3’ \\
3’ & \overset{T-----ACGCAC}{\text{ODN 2}} & 5’ \\
\rightarrow & \text{366 nm, 0°C} & \\
\text{ODN B} & \\
5’ & \overset{CNVK}{\text{GCGTG}} & 3’ \\
3’ & \overset{T-----ACGCAC}{\text{ODN 2}} & 5’ \\
\end{align*}
\]

Figure S2. HPLC analysis of the irradiated ODN 3 in the presence of ODN 2. 2’-Deoxyuridine (dU) was used as an internal standard.
**Figure S3.** (a) HPLC analysis of products during enzymatic digestion process of ODN A, (b) UV spectrum of $^{CNV}K<>T$ photoadduct.

**Figure S4.** (a) HPLC analysis of products during enzymatic digestion process of ODN B, (b) UV spectrum of $^{CNV}K<>T$ photoadduct.
**Figure S5.** Melting curves: (a) the duplex ODN 1/ODN 2 and the end-capped ODN A; (b) the duplex ODN 3/ODN 2 and the end-capped ODN B; (c) ODN 9.

**Figure S6.** CD spectra: (a) the duplex ODN 1/ODN 2 and the end-capped ODN A; (b) the duplex ODN 3/ODN 2 and the end-capped ODN B.
Scheme S3. Photosplitting of the end-capped ODN.

Figure S7. HPLC analysis of the photosplitting of ODN A. 2'-Deoxyuridine (dU) was used as an internal standard.
Scheme S4. Photoisomerization of ODN with $^{CNVK}$.

\[
\begin{array}{c}
5' \quad A^{CNVK}GCGTG \quad 3' \\
\xrightarrow{312 \text{ nm}, 60 \degree C} \\
\xleftarrow{\text{ODN 1: cis-isomer}}
\end{array}
\]

Figure S8. HPLC analysis of A) ODN 1 and B) ODN 1(cis-isomer). 2’-Deoxyuridine (dU) was used as an internal standard. C) Plot of %cis vs. irradiation time: ODN 1 (filled symbols) and ODN 1(cis-imer) (open symbols).
Scheme S5. Photosplitting of the end-capped ODN.

\[ \text{ODN B} \xrightarrow{312 \text{ nm}, 60 \degree C} \text{ODN 3} \]

Figure S9. HPLC analysis of the photosplitting of ODN B. 2’-Deoxyuridine (dU) was used as an internal standard.
Scheme S6. Photochemical 3'-end capping of ODNs with $^{CNV}_K$.

$$
\text{ODN 4} \quad \text{366 nm, 0 °C} \quad \text{ODN C}
$$

Figure S10. HPLC analysis of the irradiated ODN 4 in the presence of ODN 5. 2'-Deoxyuridine (dU) was used as an internal standard.
Scheme S7. Photochemical 3’-end capping of ODNs with $^{CNV}K$.

Figure S11. HPLC analysis of the irradiated ODN 4 in the presence of ODN 6. 2’-Deoxyuridine (dU) was used as an internal standard.
Figure S12. (a) HPLC analysis of products during enzymatic digestion process of ODN C, (b) UV spectrum of \( \text{CNV}K<>T \) photoadduct.

Figure S13. (a) HPLC analysis of products during enzymatic digestion process of ODN D, (b) UV spectrum of \( \text{CNV}K<>T \) photoadduct.
**Figure S14.** Melting curves: (a) the duplex ODN 4/ODN 5 and the end-capped ODN C; (b) the duplex ODN 4/ODN 6 and the end-capped ODN D; (c) ODN 10.

**Figure S15.** CD spectra: (a) the duplex ODN 4/ODN 5 and the end-capped ODN C; (b) the duplex ODN 4/ODN 6 and the end-capped ODN D.
Scheme S8. Photosplitting of the end-capped ODN.

$$\text{ODN C} \quad \xrightarrow{\text{312 nm, 60 °C}} \quad \text{ODN 4}$$

Figure S16. HPLC analysis of the photosplitting of ODN C. 2’-Deoxyuridine (dU) was used as an internal standard.
Scheme S9. Photoisomerization of ODN with $^{\text{CNVK}}$.

$$\text{ODN 4} \quad \text{312 nm, 60 °C} \quad \text{TDGTA}^{\text{CNVK}} \quad \text{ODN 4: cis-isomer}$$

Figure S17. HPLC analysis of A) ODN 4 and B) ODN 4(cis-isomer). 2’-Deoxyuridine (dU) was used as an internal standard. C) Plot of %cis vs. irradiation time: ODN 4 (filled symbols) and ODN 4(cis-imer) (open symbols).
Scheme S10. Photosplitting of the end-capped ODN.

Figure S18. HPLC analysis of the photosplitting of ODN D. 2′-Deoxyuridine (dU) was used as an internal standard.
**Scheme S11.** Photochemical doubly end capping of ODNs with \(^{CNVK}\).

![Scheme S11](image)

**Figure S19.** 16% PAGE of photoreversible end capping of Cy3-labeled ODN. Lane 1: duplex ODN 7/ODN 8 labeled with Cy3; lane 2: 366 nm irradiation of lane 1 for 40 s, 92% yield; lane 3: 312 nm irradiation of lane 2 for 90 s, 83% yield.

![Figure S19](image)

**Figure S20.** Melting curves: the duplex ODN 7/ODN 8 and the end-capped ODN E. \(T_m\) values of the duplex ODN 7/ODN 8 and the end-capped ODN E were measured in 50 mM sodium cacodylate buffer (pH 7.0) and 5 mM sodium chloride.

![Figure S20](image)
Figure S21. CD spectra: the duplex ODN 7/ODN 8 and the end-capped ODN E.
Figure S22. (a) Molecular modeling of stacked geometry in the end capped ODN A. (b) Molecular modeling of stacked geometry in the end capped ODN C. Yellow, and green molecules are T, and $^{CN}$K, respectively. (c) Proposed structure of $^{CN}$K<>T photoadduct.