

Supplemental Table 1. T_m s of triplexes formed from X^{mT}_{13} and various duplex targets. ^[a]

Duplex target ^[b]	$T_m / ^\circ\text{C}$		$\Delta T_m / ^\circ\text{C}$ ^[c]
	<i>trans</i> ^[d]	<i>cis</i>	
5'-t/a	30.2 (22.5)	10.7	19.5
5'-a/t	30.8 (24.6)	14.4	16.4
5'-g/c	22.5 (14.0)	0.0	22.5
5'-c/g	26.1 (17.6)	4.5	21.5
3'-g/c	35.1 (29.4)	20.1	15.0
3'-c/g	28.5 (23.4)	11.7	16.8

Sequences of the duplex targets

5'-t/a

5'-CGTCGGTT-t-AAAAAAAAAAAAAAAA-TTTCGTGGC-3'
 3'-GCAGCCAA-a-TTTTTTTTTTTTTT-AAAGCACCG-5'

5'-g/c

5'-CGTCGGTT-g-AAAAAAAAAAAAAAAA-TTTCGTGGC-3'
 3'-GCAGCCAA-c-TTTTTTTTTTTTTT-AAAGCACCG-5'

3'-g/c

5'-CGTCGGTTT-AAAAAAAAAAAAAAAA-g-TTCGTGGC-3'
 3'-GCAGCCAAA-TTTTTTTTTTTTTT-c-AAGCACCG-5'

5'-a/t

5'-CGTCGGTT-a-AAAAAAAAAAAAAAAA-TTTCGTGGC-3'
 3'-GCAGCCAA-t-TTTTTTTTTTTTTT-AAAGCACCG-5'

5'-c/g

5'-CGTCGGTT-c-AAAAAAAAAAAAAAAA-TTTCGTGGC-3'
 3'-GCAGCCAA-g-TTTTTTTTTTTTTT-AAAGCACCG-5'

3'-c/g

5'-CGTCGGTTT-AAAAAAAAAAAAAAAA-c-TTCGTGGC-3'
 3'-GCAGCCAAA-TTTTTTTTTTTTTT-g-AAGCACCG-5'

^{a)} $[T_{13}] = [X^{mT}_{13}] = [\text{duplex target}] = 2.0 \mu\text{M}$, $[\text{MgCl}_2] = 0.2 \text{ M}$, at pH 7.0 (10 mM HEPES buffer).

^{b)} The difference among the 31 mer duplex targets is the base pair next to the end of T_{13}/A_{13} part. For example, target 5'-g/c means that the base pair just next to the end of T_{13}/A_{13} part is GC, and the base G is at 5'-end direction of the A_{13} strand. Target 3'-c/g means that the base pair just next to the end of T_{13}/A_{13} part is CG, but the base C is at 3'-end direction of the A_{13} strand.

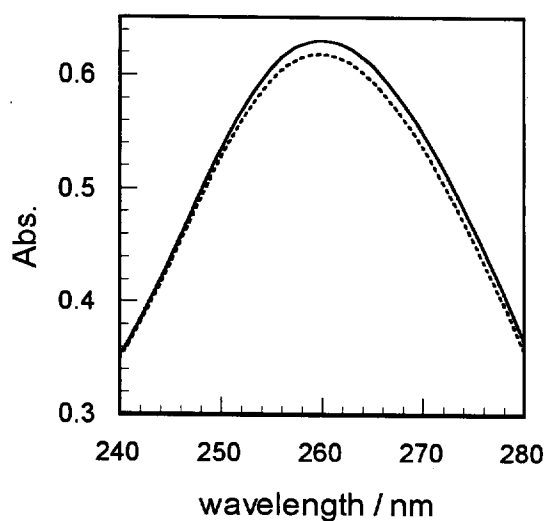
^{c)} Change of T_m induced by *cis*→*trans* isomerization

^{d)} Parentheses show the T_m s of triplexes between natural T_{13} and duplex targets.

Supplemental Table 2. The MALDI-TOFMS results of modified oligonucleotides.

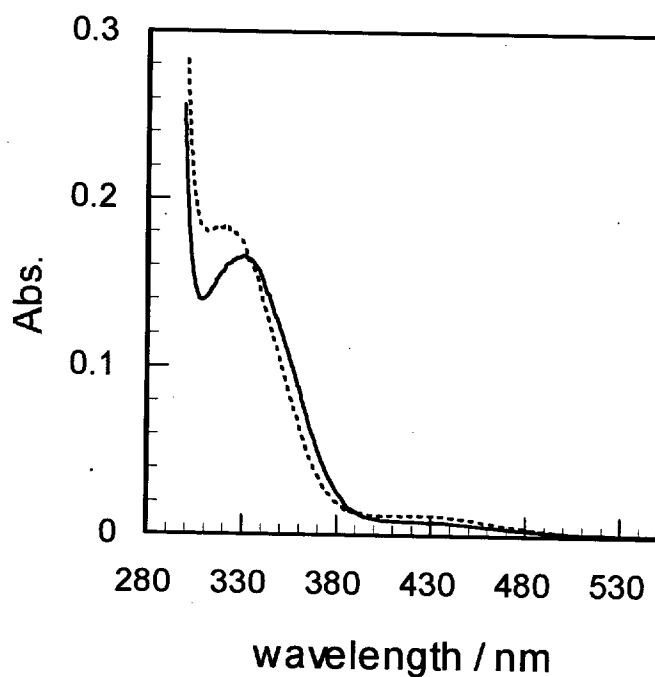
Sequence	Obsd.		Calcd.
	Polar fraction	Less polar fraction	
X ^p T ₁₃ :		4264.3	4264.7
TX ^p T ₁₂ :	4266.4	4264.4	4264.7
T ₂ X ^p T ₁₁ :	4265.2	4262.9	4264.7
T ₃ X ^p T ₁₀ :	4265.3	4263.5	4264.7
T ₄ X ^p T ₉ :	4262.0	4264.3	4264.7
T ₅ X ^p T ₈ :	4263.9	4267.6	4264.7
T ₆ X ^p T ₇ :	4265.2	4264.2	4264.7
T ₇ X ^p T ₆ :	4261.8	4264.6	4264.7
X ^p T ₆ X ^p T ₇ :	4642.6	4638.2	4639.8
T ₁₃ X ^p :		4267.4	4264.7
X ^m T ₁₃ :		4264.1	4264.7
TX ^m T ₁₂ :	4264.0	4263.1	4264.7
T ₂ X ^m T ₁₁ :	4264.1	4266.6	4264.7
T ₆ X ^m T ₇ :	4266.0	4267.1	4264.7
T ₁₃ X ^m :		4265.9	4264.7
X ^m T ₁₀ C ₃ :		4222.5	4219.7
X ^m T ₁₁ C ₃ :		4525.9	4523.7

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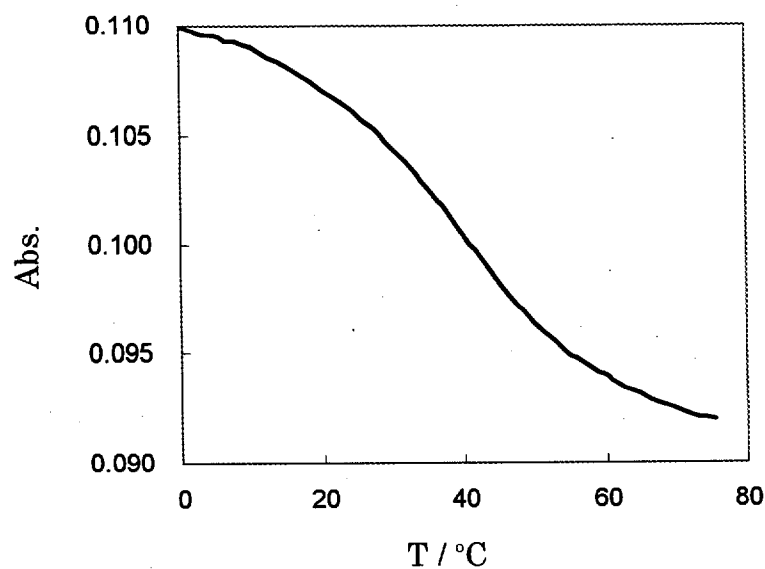


Supplemental Figure 1. Hyperchromicity at 260 nm of $X^mT_{13}/a/t$ triplex caused by the *trans*→*cis* isomerization of azobenzene at 29 °C. The dotted and solid lines are the spectra before and after UV light irradiation, respectively.

$[X^mT_{13}] = [a/t] = 10 \mu\text{M}$, $[\text{MgCl}_2] = 0.2 \text{ M}$, at pH 7.0 (10 mM HEPES buffer). T_m s of *trans*- and *cis*- $X^mT_{13}/a/t$ triplex are 37.9 °C and 20.6 °C, respectively. UV irradiation was carried out at the averaged temperature of the T_m s of *trans*- (37.9 °C) and *cis*-form (20.6 °C).



Supplemental Figure 2. UV-Vis spectra of the *trans*-X^mT₁₃/a/t at 65 °C (dotted line, $\lambda_{\text{max}} = 322$ nm) and 0 °C (solid line, $\lambda_{\text{max}} = 331$ nm). $[\text{X}^{\text{m}}\text{T}_{13}] = [\text{a/t}] = 10 \mu\text{M}$, $[\text{MgCl}_2] = 0.2 \text{ M}$, at pH 7.0 (10 mM HEPES buffer). T_{m} s of *trans*- and *cis*-X^mT₁₃/a/t triplex are 37.9 °C and 20.6 °C, respectively.



Supplemental Figure 3. Melting curve for the triplex *trans*- $X^mT_{13}/a/t$ monitored at 355 nm. The T_m was determined from this curve as 38.5 °C, which is almost the same as that determined at 280 nm (T_m at 280 nm = 37.9 °C).

[X^mT_{13}] = [a/t] = 10 μ M, [MgCl₂] = 0.2 M, at pH 7.0 (10 mM HEPES buffer).