Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Construction of photoresponsive RNA for photoswitching RNA hybridization

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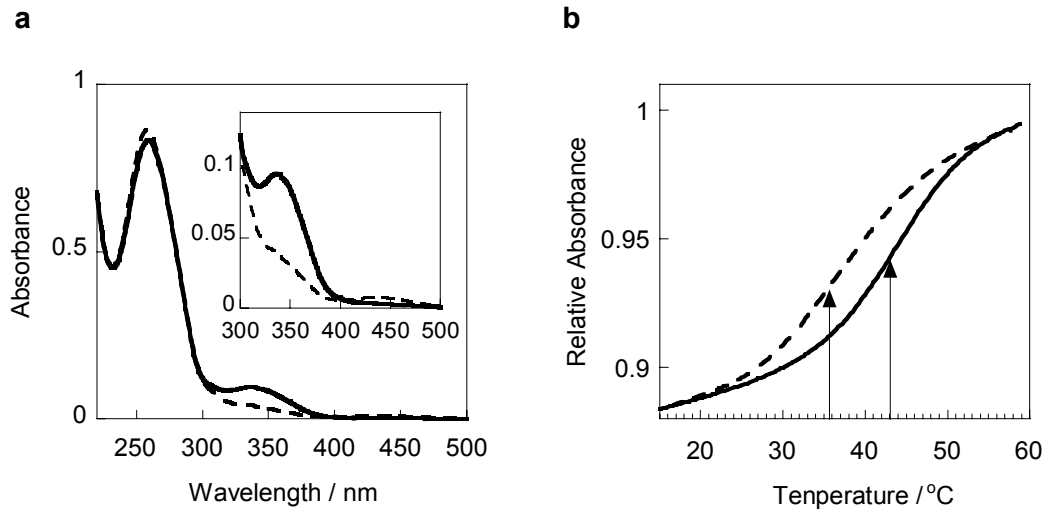
Supplemental Table S1. Thermodynamic parameters for the formation of RNA/RNA duplexes.

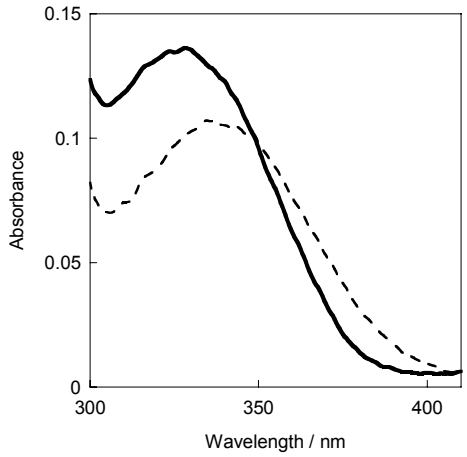
Duplex	T_m / °C [a]	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1} K^{-1})	ΔG^o [b] (kJ mol^{-1})
R_nG/R_cC	**50.7**	**-355**	**-987**	**-48.6**
***trans*-$R_{a1}G/R_cC$**	**48.8**	**-300**	**-825**	**-44.6**
***cis*-$R_{a1}G/R_cC$**	**36.5**	**-265**	**-742**	**-34.8**

[a] Conditions: 100 mM NaCl, 10 mM phosphate buffer (pH 7.0); T_m was measured at the following concentrations of RNA: 0.25, 0.5, 1.0, 2.5, and 5 μM. [b] Here the data at 37 °C (310 K) are shown.

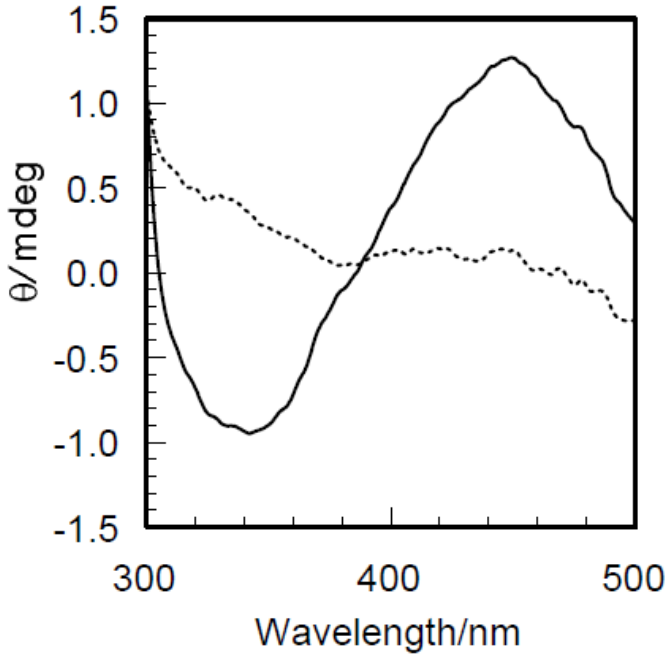
Thermodynamic parameters were obtained by measuring the T_m of duplexes at various concentrations. For *trans*-**R_XG/R_cC**, *cis*-**R_XG/R_cC**, and **R_nG/R_cC**, the changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) during duplex formation are shown in Table 2. The exothermic change ($-\Delta H°$) for *trans*-**R_XG/R_cC** was 35 kJ mol^{-1} more than that for *cis*-**R_XG/R_cC**, indicating that the stability difference between the *trans* and *cis* forms was mainly due to their difference in $\Delta H°$. On the other hand, the $-\Delta H°$ for *trans*-**R_XG/R_cC** was 55 kJ mol^{-1} less than that for the native RNA/RNA duplex **R_nG/R_cC**, demonstrating that even *trans*-azobenzene could not stack well with adjacent base pairs. These results support our analysis of the destabilization effect of *trans*-azobenzene on RNA/RNA duplexes.



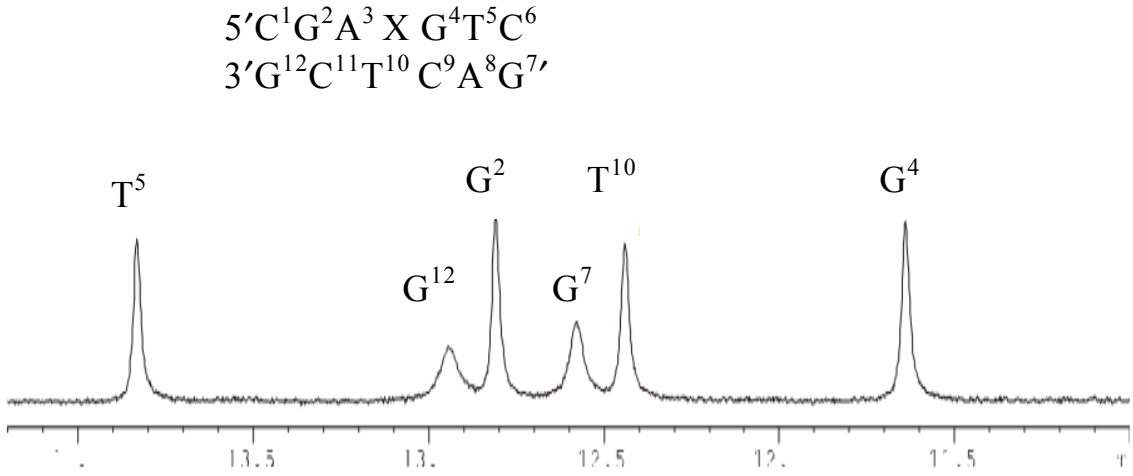
Supplemental Fig. S2. UV-Vis spectra (a) and melting curves (b) of $\mathbf{D_XG/D_cC}$ with *trans*-azobenzene (solid line) and *cis*-azobenzene (dotted line). [DNA] = 5 μM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer)..



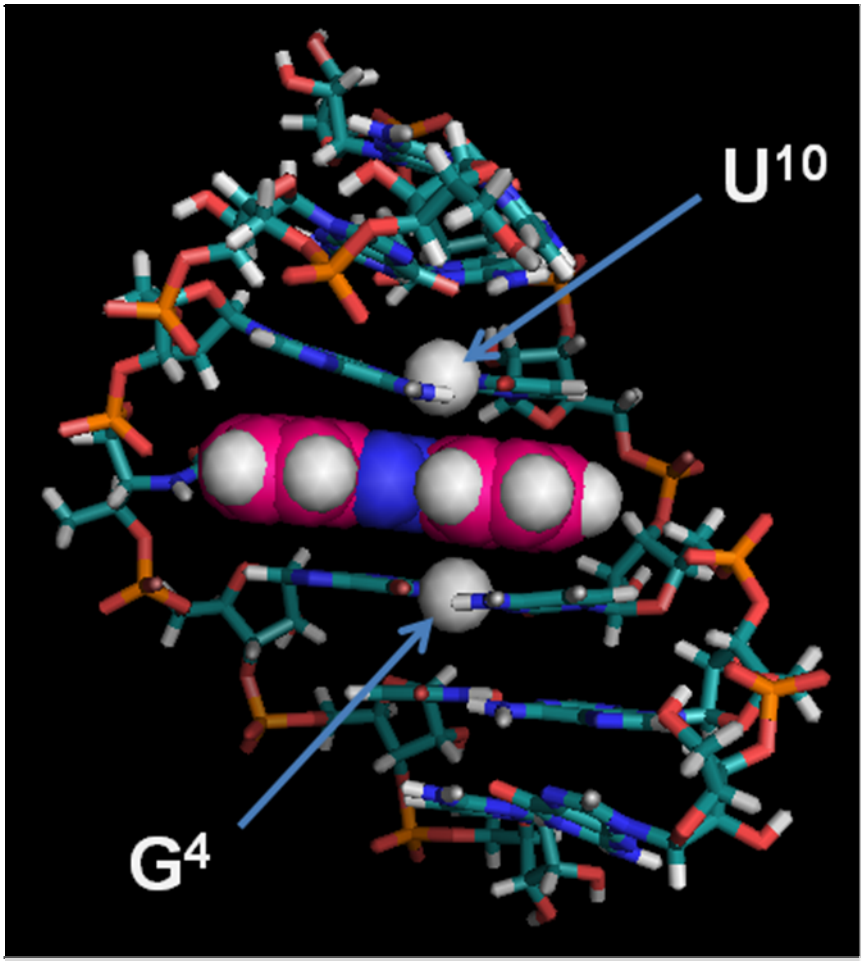
Supplemental Fig. S3. UV/Vis spectra of introduced azobenzene in $\mathbf{R_XG}$ at 80 ^{o}C (solid line) and 0 ^{o}C (dotted line) in the presence of complementary RNA $\mathbf{R_cC}$. A red shift was induced by RNA/RNA duplex formation. The λ_{max} of azobenzene at 80 ^{o}C was 330 nm whereas λ_{max} at 0 ^{o}C was 340 nm. [RNA] = 5 μM, [NaCl] = 100 mM, pH 7.0 (10 mM phosphate buffer)



Supplemental Fig. S4. CD spectra of DNA/DNA duplex (5′-GCGAXGTCG-3′/3′-CGCTCAGC-5′) involving *trans*-azobenzene at 10 °C (solid lines) and 70 °C (dotted lines). [DNA] = 5 μM, [NaCl] = 100 mM, pH7.0 (10 mM phosphate buffer).
(Asanuma, T. Takarada, T. Yoshida, D. Tamaru, X. Liang, M. Komiyama, *Angew. Chem., Int. Ed.* **2001**, *40*, 2671-2673.)



Supplemental Fig. S5. 1D ^{1}H-NMR spectrum of DNA/DNA duplex (5′-CGAXGTC-3′/3′-GCTCAG-5′) involving *trans*-azobenzene. [DNA] = 1.0 mM, [NaCl] = 200 mM, pH7.0 (20 mM phosphate buffer).



Supplemental Fig. S6. Structure of NMR-R_x/NMR-R_c duplex involving azobenzene moiety obtained from the computer modeling with the Insight II/Discover 98.0 program package. The azobenzene is highlighted in CPK (space-filling) model. The imino protons of U^{10} and G^4 are also high-lighted.