Supporting Information

Activation and Alteration of Base Selectivity by Metal Cations in the Functionality-Transfer Reaction for RNA Modification

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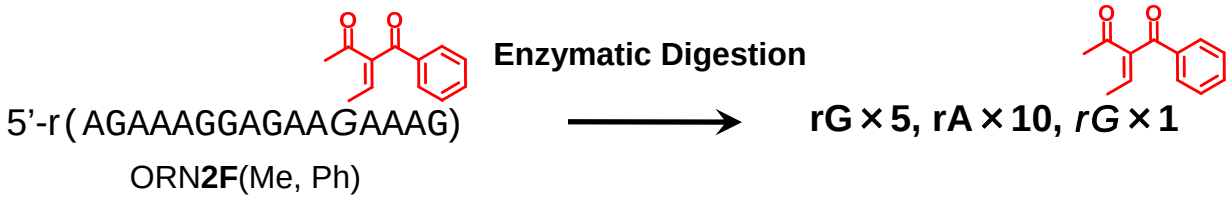
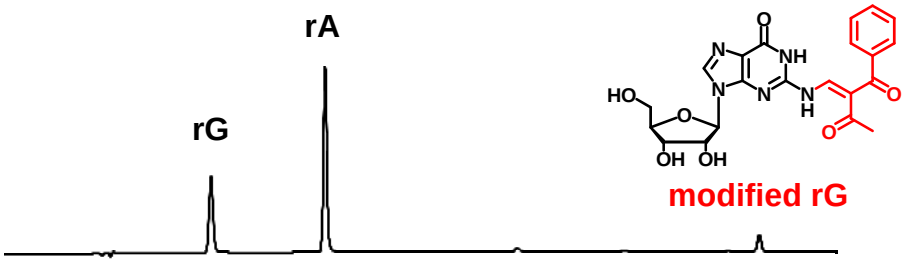


Transfer modified ORN**2F** (10 μM) was hydrolyzed with BAP (30 U/ml) and SVPD (2.0 U/ml) at 37°C for 1h, and the mixture was analyzed by HPLC (Column: SHISEIDO C18, 4.6 x 250 mm; Solvent: A: 50 mM $HCOONH_4$ Buffer, B: CH_3CN, B: 5% to 40% /30 min, linear gradient; Flow rate: 1.0 ml/min; monitored by UV detector at 254 nm).

➢ **Hydrolysate of the Ni^{2+}-activated transfer reaction product**



➢ **Hydrolysate of the transfer reaction product at pH 9.6**

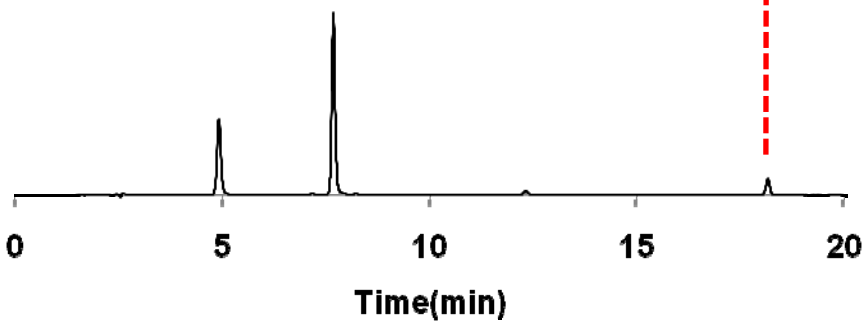


Figure 9S. HPLC analysis of the hydrolysates of the modified ORN2F(Me, Ph). The modified rG was isolated and subjected to ESI-HRMS measurements (calcd for $C_{21}H_{21}N_5O_7$ $(M+Na)^+$: 478.1333, found: 478.1351). Determination of the 2-amino modified structure of the transfer reaction at pH 9.6 has been discussed in the previous study (*19*).

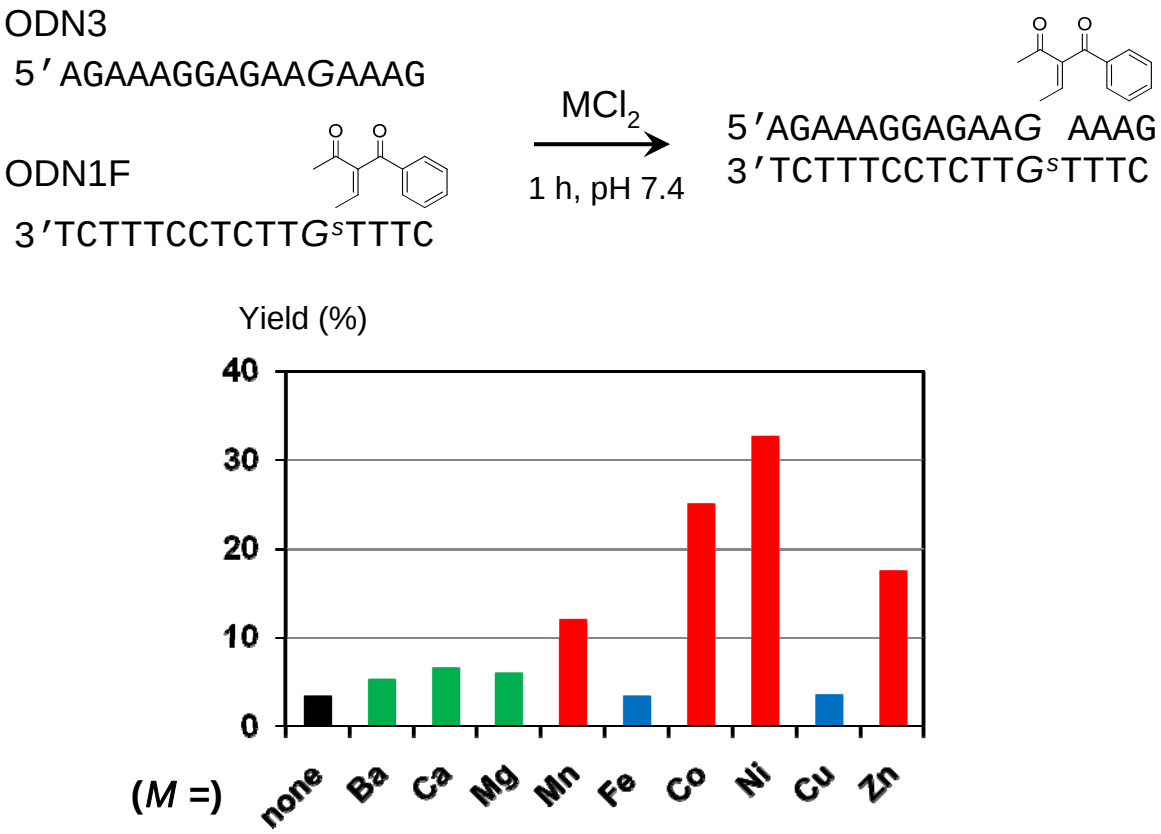


Figure 10S. Metal cation effect on the functionality transfer reaction with DNA substrate. The transfer reactions were performed by using 15 μM of *S*-functionalized ODN1F-G^S(Me, Ph) and 10 μM of the target ODN3 (G) in 50 mM MES buffer containing 100 mM NaCl in the presence of 1 mM MCl_2 at pH 7.4 for 1h, and followed by HPLC.

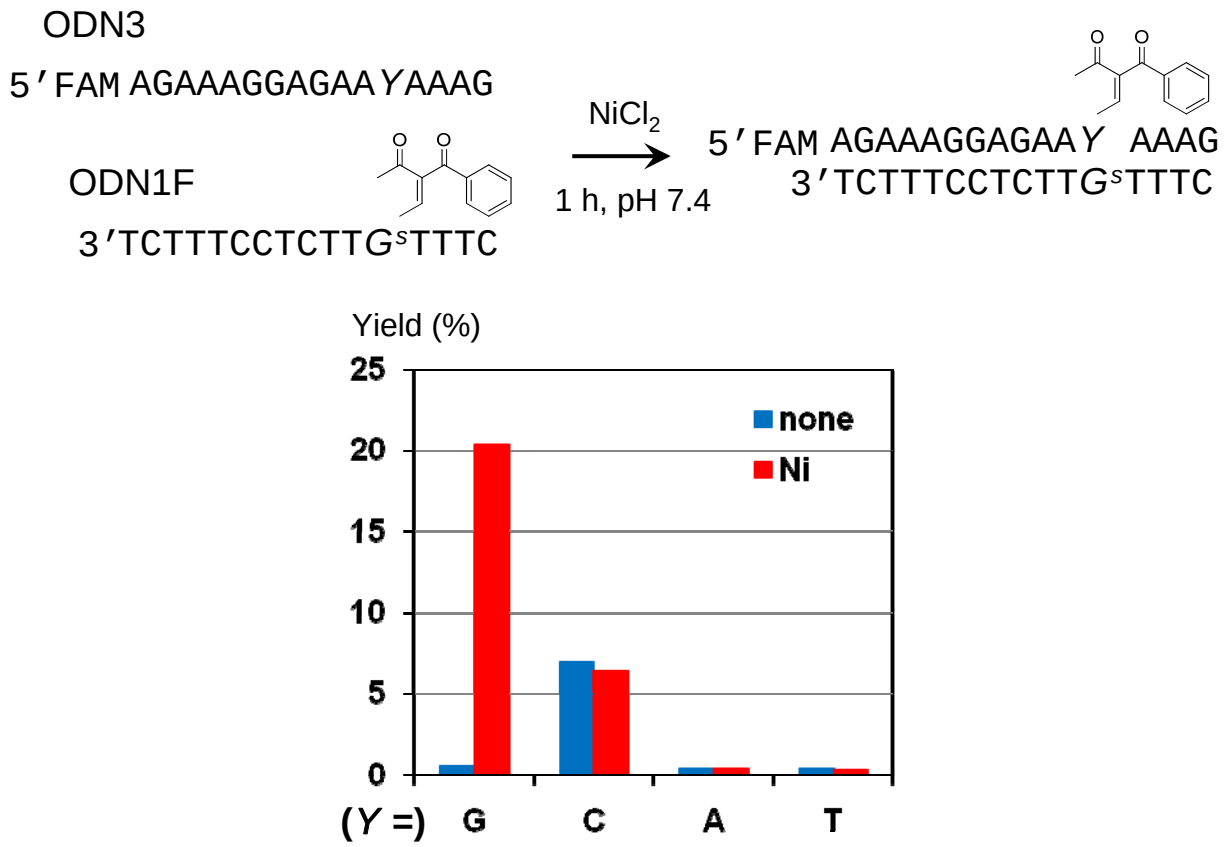


Figure 11S. Base selectivity of transfer reaction with DNA substrates in the presence of $NiCl_2$. The transfer reactions were performed by using 1.5 μM of *S*-functionalized ODN1-G^{S}(Me, Ph) and 1.0 μM of the target ODN3 (Y) in 50 mM MES buffer containing 100 mM NaCl at pH 7.4 for 1h, and followed by HPLC (monitored by monitoring the FAM fluorescence). Blue bars indicate the reaction yield in the absence of $NiCl_2$, and red bars indicate the reaction yield in the presence of 1 mM $NiCl_2$.

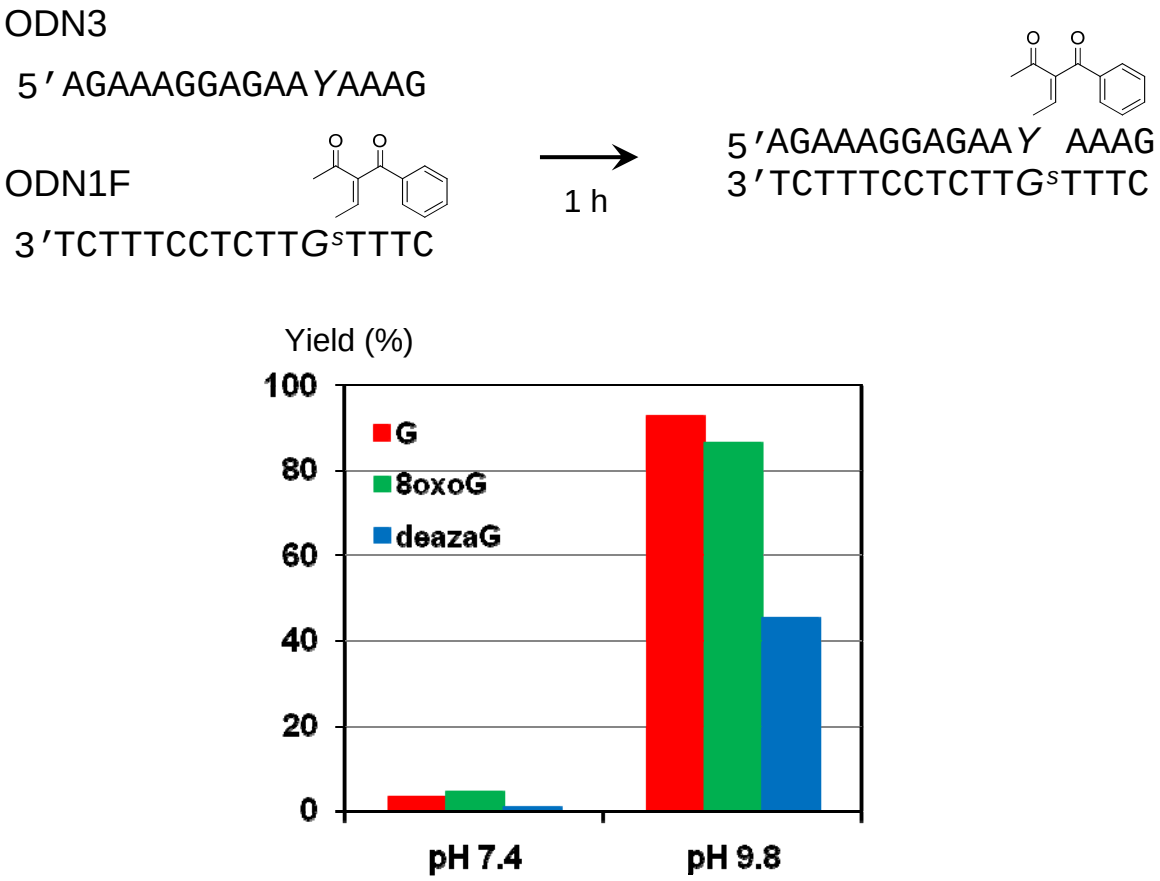


Figure 12S. Comparison of the reactivity of the guanine analogs under alkaline conditions. The transfer reactions were performed by using 15 μM of *S*-functionalized ODN1F-G^{S}(Me, Ph) and 10 μM of the target ODN3 (Y) in 50 mM carbonate buffer containing 100 mM NaCl at pH 9.8 for 1h, and followed by HPLC.

Table 1S. MALDI-TOF/MS Data of all ODN and ORN compounds used in this study.

DNA or RNA	5' Label	X or Y	Calcd ([M-H]$^-$)	Found
ODN**1**		X = G^S	4767.8	4766.5
ODN**1F**		X = G^S(Me, Ph)	4939.7	4939.4
ODN**1F**		X = G^S(H, Ph)	4897.8	4898.8
ORN**2**		Y = rG	5297.8	5297.8
ORN**2**	FAM	Y = rG	5835.9	5835.9
ORN**2**	FAM	Y = rC	5795.9	5795.1
ORN**2**	FAM	Y = rA	5819.9	5819.5
ORN**2**	FAM	Y = rU	5796.9	5796.5
ORN**2F**		Y = rG(Me, Ph)	5469.8	5469.9
ODN**3**	FAM	Y = dG	5579.1	5579.5
ODN**3**	FAM	Y = dC	5539.1	5538.7
ODN**3**	FAM	Y = dA	5563.1	5563.5
ODN**3**	FAM	Y = dT	5554.1	5553.7
ODN**3**		Y = dG	5041.9	5041.6
ODN**3**		Y = 8oxodG	5057.9	5056.8
ODN**3**		Y = deazadG	5040.1	5040.1
ODN**3F**		Y = dG(Me, Ph)	5214.0	5213.6
ODN**3F**		Y = 8oxodG(Me, Ph)	5230.0	5229.9
ODN**3F**		Y = deazadG(Me, Ph)	5212.1	5212.4