Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Drastic enhancement of excess electron-transfer efficiency through DNA by inserting consecutive 5-phenylethynyl-2'-deoxyuridines as a modulator

Makiko Tanaka[*a], Kazuhiro Oguma[a,b], Yoshio Saito[b] and Isao Saito[*a]

[a]*NEWCAT Institute, School of Engineering, Nihon University, Koriyama, Fukushima 963-8642, Japan*

[b]*Department of Chemical Biology and Applied Chemistry, School of Engineering, Nihon University, Koriyama, Fukushima 963-8642, Japan*

Experimental

Oligodeoxynucleotide synthesis and characterization. Oligodeoxynucleotides (ODNs) were prepared using phosphoramidite chemistry on an ABI DNA Synthesizer. All phosphoramidites and reagents for DNA synthesis were purchased from Glen Research with the exception of the ^{Ph}U phosphoramidite. 5-Br-dU phosphoramidite for ^{Br}U and Pyrene-dU-CE Phosphoramidite for ^{Py}U were also purchased from Glen Research. 5-(Phenylethynyl)-2'-deoxyuridine (^{Ph}U) was prepared according to the literature.[1] Calf intestinal alkaline phosphate (Promega), Crotalus adamanteus venom phosphodiesterase I (USB), and Penicillium citrinum nuclease P1 (Yamasa Shoyu) were used for the enzymatic digestion of oligonucleotides. All aqueous solutions utilized purified water (Millipore, Milli-Q spUF). Reversed-phase HPLC was performed on CHEMCOBOND 5-ODS-H columns (10x150 mm, 4.6x150 mm) with a JASCO Chromatograph, Model UV-2075 plus at 260 nm. Mass spectra of ODNs purified by HPLC were determined with a MALDI-TOF mass spectrometer.

UV-vis, and fluorescence measurements. Absorption spectra were obtained using a Shimadzu UV-2550 spectrophotometer at room temperature using 1 cm path length cell. Fluorescence spectra were recorded on a Shimadzu spectrofluorophotometer (RF-5300PC).

Photoreduction Experiments. Aliquots (10 μM DNA, 100 mM NaCl, 50 mM sodium phosphate buffer, pH 7.0, total volume 30 μL) for irradiation were prepared by annealing equimolar amounts of the desired DNA complements. Aliquots were then transferred to a lucent cell sealed with a rubber septum and deoxygenated with Argon for 20 min. Monochromatic light was irradiated with a Xe lamp (300 W; Asahi Spectra Co. Ltd.; MAX-303) equipped with high concentrating lens unit (ϕ 2.5), high quality band-pass filter (LX0400) for 400 nm, and ND filter (5-100%). The shutter timer is variable from 0.5 to 99999.9sec. After irradiation at 400 nm, duplex samples were digested by 37 ^{o}C incubation with Calf intestinal alkaline phosphate, Crotalus adamanteus venom phosphodiesterase I, and Penicillium citrinum nuclease P1 for 12-14 h in order to yield the free nucleosides, and the samples were analyzed by reversed

phase HPLC CHEMCOBOND 5-ODS-H column (4.6x150 mm) at 290 nm. The percentage decomposition of ^{Br}U was determined using dC as an internal standard for all HPLC traces. Irradiations were repeated at least three times and the results averaged.

Electrochemical Measurements. Measurements of the cyclic voltammetry (CV) were performed at 298 K, using a BAS 100W electrochemical analyzer in a deaerated DMF containing 0.10 M $TBAPF_6$ (tetra-*n*-butylammonium hexafluorophosphate) as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to the $Ag/AgNO_3$ (1.0×10^{-2} M) reference electrode. The E_{red} values (vs $Ag/AgNO_3$) are converted to those vs SCE by ferrocene (0.51V vs SCE in DMF)[2] as an internal reference. All electrochemical measurements were carried out under an atmospheric pressure of argon.

References

1 R. H. E. Hudson and A. Ghorbani-Choghamarani, *Org. Biomol. Chem.*, 2007, **5**, 1845-1848.

2 D. Dubois, G. Moninot, W. Kutner, M. T. Jones and K. M. Kadish, *J. Phys. Chem.*, 1992, **96**, 7137-7145.

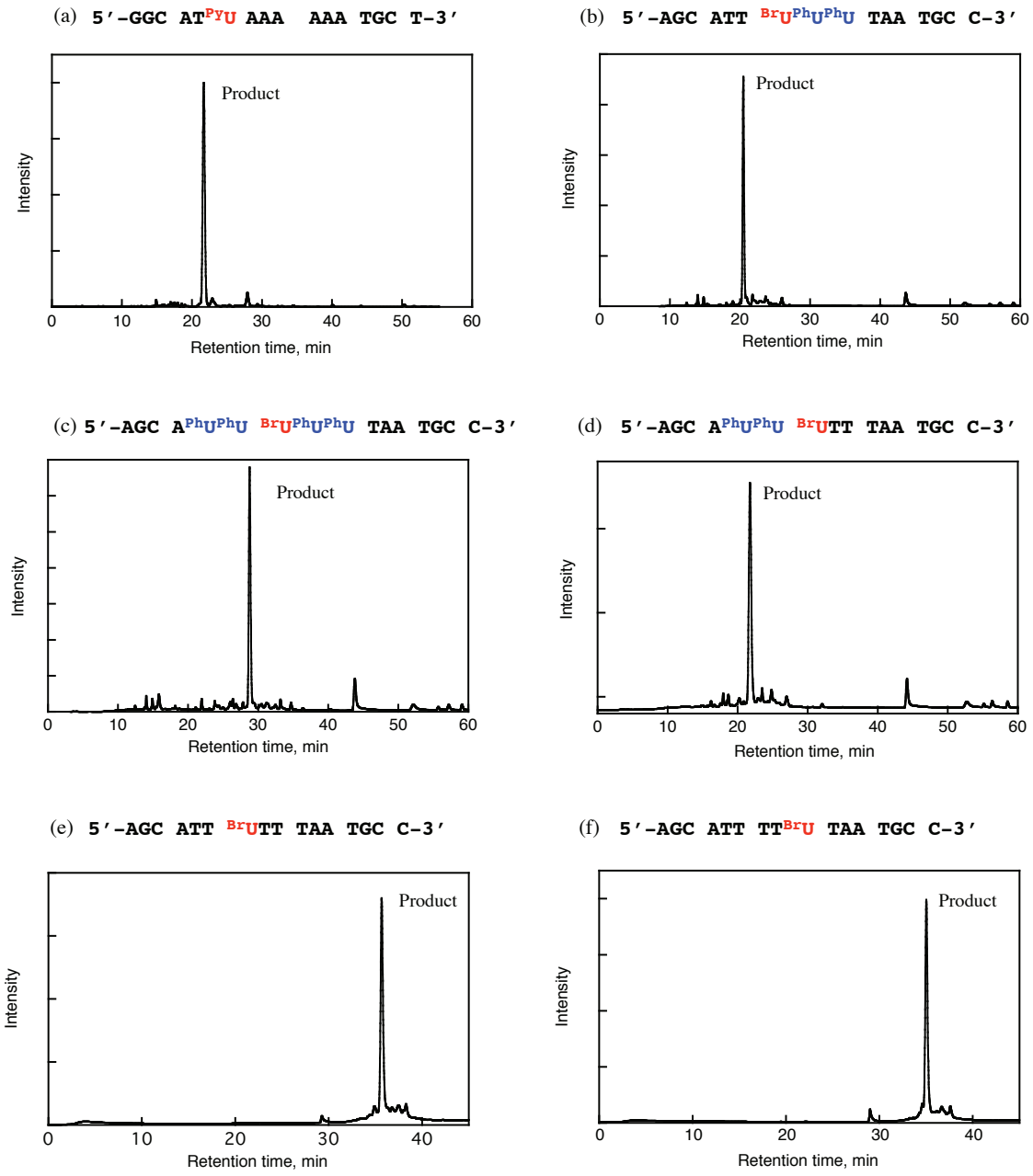

Fig. S1 HPLC profile of crude reaction mixture. HPLC analysis was carried out on a CHEMCOBOND 5-ODS-H column eluted with 0.05 M ammonium formate buffer containing acetonitrile. Gradient: 3-30 % over 60 min for (a), 3-40 % over 60 min for (b), (c) and (d), 3-20 % over 45 min for (e) and (f). The largest peaks were collected.

Table S2. m/z values for modified ODNs determined by MALDI-TOF mass spectrometry.

Sequence	Mass found	Mass calcd ($[M+H]^+$)
5′-GGC AT^{PyU} AAA AAA TGC T-3′	5123.4	5124.5
5′-AGC ATT $^{Br}U^{Ph}U^{Ph}U$ TAA TGC C-3′	5085.1	5084.3
5′-AGC A$^{Ph}U^{Ph}U$ $^{Br}U^{Ph}U^{Ph}U$ TAA TGC C-3′	5257.8	5256.5
5′-AGC A$^{Ph}U^{Ph}U$ ^{Br}UTT TAA TGC C-3′	5084.3	5084.3
5′-AGC ATT ^{Br}UTT TAA TGC C-3′	4913.3	4912.1
5′-AGC ATT TT^{Br}U TAA TGC C-3′	4913.2	4912.1

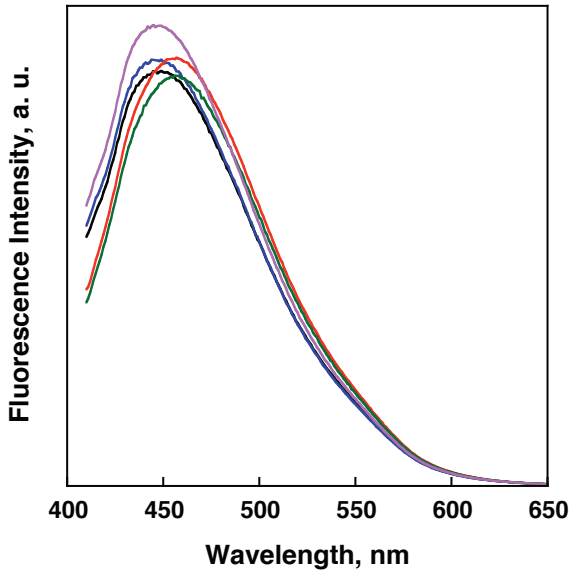

Fig. S3 Fluorescence spectra of DNA I (blue line), II (green line), III (solid red line), IV (purple line), and V (black line); 2.0 μM duplex, 50 mM phosphate buffer, pH 7.0, 100 mM NaCl. Excitation wavelength is 400 nm.

Table S4. Sequence and melting temperatures for DNA duplexes containing a single ^{Ph}U base and a different counter base (A, T, G, C).

DNA sequence	T_m, °C[a]
5′-CGC AAT ^{Ph}UTA ACG C-3′ 3′-GCG TTA AAT TGC G-5′	**50.6**
5′-CGC AAT ^{Ph}UTA ACG C-3′ 3′-GCG TTA TAT TGC G-5′	39.9
5′-CGC AAT ^{Ph}UTA ACG C-3′ 3′-GCG TTA GAT TGC G-5′	40.4
5′-CGC AAT ^{Ph}UTA ACG C-3′ 3′-GCG TTA CAT TGC G-5′	40.2
5′-CGC AAC ^{Ph}UCA ACG C-3′ 3′-GCG TTG AGT TGC G-5′	**62.5**
5′-CGC AAC ^{Ph}UCA ACG C-3′ 3′-GCG TTG TGT TGC G-5′	50.6
5′-CGC AAC ^{Ph}UCA ACG C-3′ 3′-GCG TTG GGT TGC G-5′	50.1
5′-CGC AAC ^{Ph}UCA ACG C-3′ 3′-GCG TTG CGT TGC G-5′	48.2

[a] Experimental conditions: [DNA duplex] = 2.5 μM in 50 mM sodium phosphate, pH7.0, 100mM NaCl. T_m is determined by monitoring the UV absorption at 260 nm.