Supporting Information

Unexpectedly Large Water-proton Relaxivity of TEMPO Incorporated into Micelle-Oligonucleotide

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Contents

1.

Experimental

General Methods. Infrared spectra were recorded on a JASCO 420 FT-IR spectrometer. UV-Vis spectra were recorded on a JASCO V570 spectrometer. ^{1}H NMR spectra were measured on a JEOL 270 Fourier transform spectrometer using $CDCl_3$ and CD_3OD as solvent and referenced to TMS. MALDI TOF mass (MALDI TOF MS) and ESI mass spectra (ESI MS) were recorded on a Bruker Daltonics MALDI-TOF Reflex-TOF spectrometer and Bruker Daltonics microTOF spectrometer. Melting points were obtained with a MEL-TEMP heating block and are uncorrected. DLS measurements were performed on a Zetasizer Nano ZS (Malvern Instruments Ltd.) AFM and MFM images were collected with DimensionIcon (Veeco Instruments Ltd.). Elemental analyses were performed in the Analytical Center of the Faculty of Science in Kyushu University.

Determination of Concentrations Concentrations of the samples for all oligonucleotides carrying aminoxy were estimated from the calibration curve, which was obtained by the concentration dependence of double integration of ESR signals of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO–OH) in the range of 1.0−0.1 mM. Furthermore, the concentration of the samples was also confirmed by the measurement of the absorption at 260 nm. The absorption coefficiencys, ε, of 9300 and 15300 at 260 nm for thymine and adenine, respectively, were used for the calculation.

Determination of Thermal Denaturation Temperatures (*T*m) UV-monitored denaturation experiments were conducted at 260 nm using a SHIMADZU UV-2450 spectrometer on the modified and unmodified oligonucleotides under the following conditions: phosphate buffer (10 mM, pH=7.0), NaCl (100 mM), $MgCl_2$ (50 mM). The absorption at 260 nm was followed by heating at a rate of 0.5 °C / min.

Circular Dichroism Measurements The CD spectra were recorded on a JASCO J-720W78 CD spectrometer at 25°C. Solution samples (3.3 mM) of a double strand in phosphate buffer (10 mM, pH=7.0) containing NaCl (100 mM) and $MgCl_2$ (50 mM) were used.

ESR Spectra ESR spectra were recorded on a Bruker Biospin ESR300 EPR X-band (9.4 GHz) spectrometer equipped with a microwave frequency counter. Sample solutions in phosphate buffer were placed in capillary tubes and were measured at 25 °C.

Relaxivity Measurements The spin-lattice and spin-spin relaxation rates (T_1 and T_2, respectively) were obtained on a JEOL JNM-MU25A spectrometer (25 MHz, 0.59 T). The sample solutions (ca. 0.1 − 0.7 mM) in phosphate buffer were placed in 10 mm o.d. glass tubes and were measured at 25°C. The values of relaxivity, r_1 and r_2, were calculated with equations (1) and (2).

$$1/T_1 = 1/T_0 + r_1C \qquad (1)$$

$$1/T_2 = 1/T_0 + r_2C \qquad (2)$$

, where T_0 and C are the relaxation rate in the absence of the paramagnetic species and the concentration of the paramagnetic species, respectively.

T*$_1$-weighted Images *in vitro Esr spectra of the solutions of lipid-polyTinSS and –DS in buffer were measured and their concentrations were determined from the calibration curve of ESR signal intensity. The solutions of contrast agents were diluted with buffer to 1 mM solution. By using 1 mM solution, the solutions of the given concentration were obtained. The buffer solutions of contrast agents (150 μl) were put into a polymerization chain reaction (PCR) tube cluster plate (200 μl, Simport Plastics Ltd., Beloeil, Canada), as shown in Figure S1. The PCR tube cluster plate was set in the center of the volume coil. For the comparison of the relaxivities at 7.0 and 1.0 T, the same samples in the PCR tube cluster plate were used for 7.0 and 1.0 T-MRI measurements. Sample temperature was maintained at 22.0 ± 0.5°C throughout all experiments.

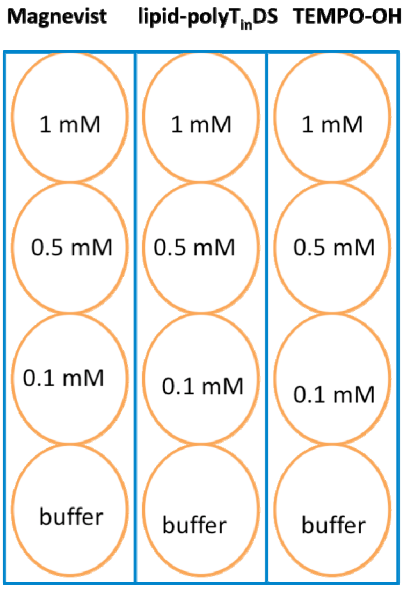


Figure S1. Samples of given concentrations aligned in the PCR tube cluster plate for the relaxivity measurements of Magnevist, lipid-polyTinDS, and TEMPO-OH for

The MRI acquisitions of contrast agents were performed on a 7.0 T-MRI scanner (Magnet: Kobelco and JASTEC, Kobe, Japan; Console: BrukerBiospin, Ettlingen, Germany) with a volume coil (35 mm inner-diameter, transmission and reception, Rapid Biomedical, Rimper, Germany) or a 1.0 T-MRI scanner (M-2, Aspect Imaging, Israel) with a volume coil (mouse body coil, transmission and reception, Aspect Imaging).

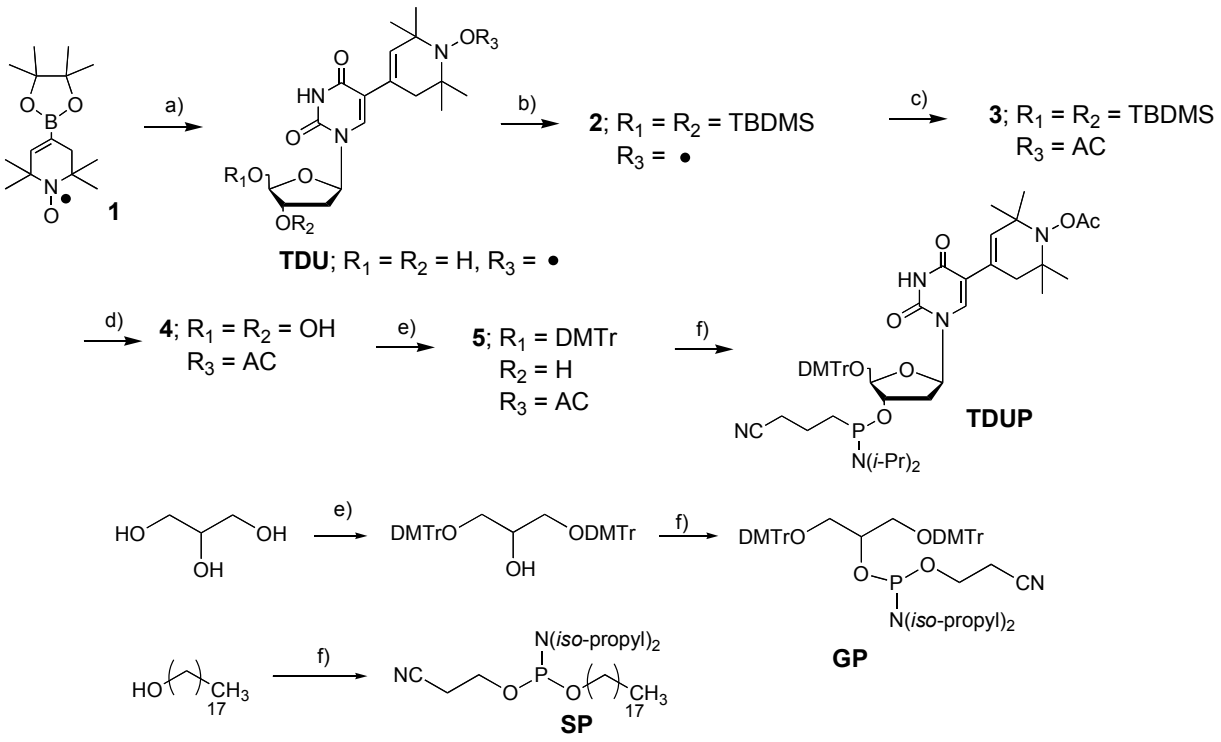
For 7.0 T-MRI scanner, horizontal single-slice T_1-weighted MR images were acquired with the following parameters: spin echo, TR/TE =250/9.6 ms, slice thickness = 2.0 mm, matrix = 256 × 256,

field of view (FOV) =38.4 × 38.4 mm^2, number of averages (NA) = 1, number of slices = 1. The total acquisition time for T_1-weighted MRI was 1.1 minute. For longitudinal relaxation time (T_1) and longitudinal relaxivity (r_1) calculations, horizontal single-slice inversion-recovery MRI was obtained using RARE (rapid acquisition with relaxation enhancement) acquisition with the following parameters: TR = 10,000 ms, TE = 10 ms, inversion time = 52, 100, 200, 400, 800, 1600, 3200, 6400 ms, matrix size = 128 × 128, FOV = 38.4 × 38.4 mm^2, slice thickness = 2.0 mm, RARE factor = 4, and NA = 1. The total acquisition time for inversion-recovery MRI was 42.7 minutes.

For 1.0 T-MRI scanner, horizontal single-slice T_1-weighted MR images were acquired with the following parameters: spin echo, TR/TE = 350/10 ms, slice thickness = 2.0 mm, matrix = 128 × 128, FOV = 42.0 × 42.0 mm^2, NA = 1, number of slices = 1.The total acquisition time for T_1-weighted MRI at 1.0 T-MRI was 0.8 minutes. For T_1 and r_1 calculations, horizontal single-slice inversion-recovery MRI was obtained using conventional spin-echo acquisition with the following parameters: TR = 10,000 ms, TE = 10 ms, inversion time = 13.2, 20, 50, 75, 100, 200, 400, 600, 800, 1000, 1200, 1600, 3200, 6400 ms, matrix size = 128 × 128, FOV = 42.0 × 42.0 mm^2, slice thickness = 2.0 mm, RARE factor = 4, and NA = 1. The total acquisition time for inversion-recovery MRI was 5 hours.

Statistics and Data Analysis T_1 maps were calculated with non-linear least squares fitting. ParaVision (BrukerBiospin), MRVision (MRVision Co., USA) and Osirix (Antoine Rosset, USA) were used to display and perform analysis on all MR images.

Materials Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2), dimethyformamide (DMF), dimethylsulfoxide (DMSO) and pyridine were distilled under high-purity N_2 after drying with calcium hydride. 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO–OH) and 5-Iodo-2'-deoxyuridine were purchased and used without purification. Abbreviations used in this work: EDC =1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, TBDMSCl = *t*-Butyldimethylsilyl chloride, TBAF = Tetrabutylammonium fluoride, DMTrCl = 4,4'-Dimethoxytrityl chloride, DMAP = 4-*N*,*N*-Dimethylaminopyridine.



a) 5-Iode-2'-deoxyuridine, $Pd(PPh_3)_4$, NaOH, MeOH, THF, water,b) TBDMS-Cl, Imidazole, DMF,
c) 1) L-ascorbic acid, CH_3OH, 2) $(CH_3)_2O$, DMAP, Imidazole, CH_2Cl_2, d) TBAF, THF, e) 1) DMTrCl, DMAP, Py.
f) *N,N*-diisopropylethylamine, 2-Cyanoethyl-*N,N,N′,N′*-tetraisopropylphosphordiamidite, CH_2Cl_2

Scheme S1. Preparation routes for **TDUP**, **GP**, and **SP**

2,2,6,6-tetramethyl-4-(4,4,5,5-tetramethyl-1,2,3-dioxaborolan-2yl)-3,6-dihydropyridin-1(2H)-yloxyl (1) This was prepared using a procedure modified from the literature.[1)] ^{1}H NMR (270 MHz, $CDCl_3$ + phenylhydrazine) δ6.26 (*s*, 1H), 2.47 (*s*, 2H), 1.46 (*s*, 6H), 1.37 (*s*, 6H), 1.28 (*s*, 12H); ESI MS: *m/z* Calcd for $[C_{15}H_{27}BNO_3Na]$ 303.2, Found 303.2 $[M+Na]^+$; ESR (CH_2Cl_2), g = 2.0084, a_N = 11.5 gauss.

5-(1-Oxy-2,2,6,6-tetramethylpiperidinyl)-2'-deoxyuridine (TDU) The solution of 5-iodo-2'-deoxyuridine (1.6 g, 4.6 mmol) dissolved in 1 : 1 mixture (286 ml) of THF and H_2O was mixed with the MeOH (124 ml) solution of **1** (2.1 g, 7.49 mmol), tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, (323 mg, 3.0 mmol%), and sodium hydroxide (2.8 g, 138 mmol). The reaction mixture was heated at 50˚C for 5 hr. under nitrogen atmosphere. After neutralization with ammonium chloride, the reaction mixture was extracted with EtOAc. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated. The crude mixture was chromatographed on silica gel with $CHCl_3$/MeOH as the eluent to give **TDU** as a pale yellow solid in 67% yield (1.2 g, 3.2 mmol). Mp (decomp.), 205°C; IR (KBr) 3493(ν_{OH}), 1718($\nu_{O=C}$)

cm^{-1}; ^1H NMR (270 MHz, CD_3OD + phenyhydradine) δ 7.96 (*s*, 1H), 6.23 (*t*, *J* = 0.2 and 0.1 Hz, 1H), 6.16 (*s*, 1H), 4.43 (*m*, 1H), 3.92(*m*, 1H), 3.78(s, 2H), 2.32 (*m*, 2H), 2.14 (*s*, 2H), 1.25 (*s*, 6H), 1.18(*s*, 6H); ESI MS: *m*/*z* Calcd for $[C_{18}H_{26}N_3O_6Na]$ 403.1719, found 403.1745$[M+Na]^+$; ESR (H_2O), *g* = 2.0087, a_N = 14.2 gauss. ; Anal Calcd for $C_{18}H_{26}N_3O_6$: C, 56.83; H, 6.89; N, 11.05%, found: C, 56.55; H, 7.02; N, 10.87%.

5-(1-Oxy-2,2,6,6-tetramethylpiperidinyl)-2'-deoxy-3',5'-bis-*O*-*tert*-butyldimethylsililuridine (2) To this solution of **TDU** (2.1 g, 5.5 mmol) dissolved in DMF (27 ml) was added TBDMSCl (2.1 g, 14.0 mmol) and imidazole (1.2 g, 17.6 mmol). The reaction mixture was stirred at room temperature for 2 hr. H_2O was added and extracted with CH_2Cl_2. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated in a vacuum. The crude residue was chromatographed on silica gel with *n*-hexane/ EtOAc as the eluent to give protected, **TDU**, **2**, as a pale yellow solid in 99% yield (3.3 g, 5.4 mmol); Mp(decomp.) 167−168°C; IR (KBr) 1707($\nu_{O=C}$) cm^{-1}; ESI MS: *m*/*z* Calcd for $[C_{30}H_{54}N_3O_6Si_2Na]$ 631.345, found 631.356 $[M+Na]^+$; Anal Calcd for $C_{30}H_{54}N_3O_6Si_2$: C, 59.17; H, 8.94; N, 6.90%, found: C, 59.01; H, 8.99; N, 6.93%.

5-(1-Acetyloxy-2,2,6,6-tetramethylpiperidinyl)-2'-deoxy-3',5'-bis-*O*-*tert*-butyldimethylsililuridine (3) L-Ascorbic acid (1.3 g, 7.2 mmol) was added to the solution of the protected uridine derivative **2** (2.7 g, 4.5 mmol) dissolved in MeOH (15 ml). The solution was stirred for 5 min. at room temperature. H_2O was added and extracted with CH_2Cl_2 three times. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated to dryness. The obtained white powder was dissolved in anhydrous CH_2Cl_2 (52 ml), and imidazole (1.6 g, 23.5 mmol) and anhydrous acetic acid (1.5 ml) were added. The reaction mixture was stirred at room temperature overnight. H_2O was added and extracted with CH_2Cl_2 three times. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated to dryness. The crude residue was chromatographed on silica gel with *n*-hexane/ EtOAc as the eluent to give protected, **TDU**, **3**, as a white solid in 75% yield (2.2 g, 3.4 mmol); Mp 159.1−160°C; IR (KBr) 1756($\nu_{O=C}$), 1714($\nu_{O=C}$) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz): δ 8.09 (*s*, 1H), 6.22 (*t*, *J* = 8.1 and 6.0 Hz, 1H), 6.10 (*s*, 1H), 4.40 (*m*, 1H), 3.96 (*m*, 1H), 3.35−3.28 (*m*, 2H), 2.35−2.28 (*m*, 2H), 2.14 (*br*, 5H), 1.33−1.19 (*m*, 12H), 0.90 (*s*, 18H), 0.09 (*s*, 6H), 0.075 (*s*, 6H); HRESI MS: *m*/*z* Calcd for $[C_{32}H_{57}N_3O_7Si_2Na]$ 674.3627, found 674.3629 $[M+Na]^+$.

5-(1-Acetyloxy-2,2,6,6-tetramethylpiperidinyl)-2'-deoxyuridine (4) TBAF (4.7 ml, 16 mmol) was added to a solution of **3** (2.1 g, 3.2 mmol) in THF (25 ml). The solution was stirred at room temperature overnight and then solvent was evaporated to the dryness. The crude residue was chromatographed on silica gel with $CHCl_3$/MeOH as the eluent to give **4** as a white solid in 97% yield (1.3 g, 3.1 mmol); Mp 104−106°C; IR (KBr) 3443(ν_{OH}), 1758($\nu_{O=C}$), 1697($\nu_{O=C}$) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.69 (*s*, 1H), 6.24 (*t*, *J* = 6.7 and 5.4Hz, 1H), 6.10 (*s*, 1H), 4.61 (*m*, 1H),

4.05−4.04(*m*, 1H), 3.98−3.83 (*m*, 2H), 2.39−2.32 (*m*, 2H), 2.17 (*s*, 2H), 2.13(s, 3H), 1.34−1.18 (*m*, 12H) ; HRESI MS: *m*/*z* Calcd for [$C_{20}H_{29}N_3O_7Na$] 446.1898, found 446.1893 $[M+Na]^+$.

5-(1-Acetyloxy-2,2,6,6-tetramethylpiperidinyl)-2'-deoxy-5'-*O*-(4,4'-diethoxytrityl)uridine (5) 4, 4'-dimethoxytrityl chloride (1.5 g, 4.4 mmol) and 4-dimethylaminopyridine (61 mg, 0.5 mmol) were added to the solution of **4** (1.2 g, 2.9 mmol) dissolved in anhydrous pyridine (7 ml). The solution was stirred for 1.5 hr. at room temperature. After quenching with MeOH, H_2O was added and extracted with CH_2Cl_2 three times. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated to dryness. Compound **5** was obtained as white solids in 56% yield (1.20 g, 0.28 mmol); Mp 118−120°C; IR (KBr) 3447(ν_{OH}), 1762($\nu_{O=C}$), 1689($\nu_{O=C}$) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ7.97 (*s*, 1H), 7.29−7.16 (*m*, 9H), 6.85−6.82 (*m*, 4H), 6.24 (*t*, 1H), 6.10 (*s*, 1H), 4.61 (*m*, 1H), 4.05−3.87 (*m*, 3H), 3.80 (*s*, 6H), 2.41−2.33 (*m*, 2H), 2.18 (*s*, 2H), 2.13 (*s*, 3H), 1.34 −1.19 (*m*, 12H); HRESI MS: *m*/*z* Calcd for [$C_{41}H_{47}N_3O_9Na$] 748.3205, found 748.3235 $[M+Na]^+$.

5-(1-Acetyloxy-2,2,6,6-tetramethylpiperidinyl)-2'-deoxy-3'-O-(2-cyanoethyl)-*N*,*N*-diisopropylphosphramidite-5'-*O*-(4,4'-diethoxytrityl)uridine (TDUP) *N*,*N*-diisopropylethylamine (0.7 ml, 4.2 mmol) was added to the solution of **5** (1.1 g, 1.5 mmol) in anhydrous CH_2Cl_2 (16 ml). The solution was stirred for 10 min in an ice bath and added to 2-cyanoethyl-*N*, *N*, *N*', *N*'-tetraisopropylphosphordiamidide (0.48 ml, 1.5 mmol). The solution was stirred for 1.5 hr. at room temperature. After quenching with aqueous 5% $NaHCO_3$ (10 ml) the organic layer was extracted with CH_2Cl_2 three time, dried over $MgSO_4$, and concentrated to dryness. The obtained pale yellow oil was chromatographed on silica gel with *n*-hexane/ EtOAc (5% Et_3N) as the eluent to give **TDUP** as a white solid in 69% yield (0.95 g, 1.0 mmol).; Mp 93−95 °C; IR (KBr) 1763($\nu_{O=C}$), 1685($\nu_{O=C}$) cm^{-1}; ^1H-NMR (270 MHz, $CDCl_3$,): δ8.14 (*s*, 1H), 7.44−7.28 (*m*, 9H), 6.84−6.81 (*m*, 4H), 6.22 (*m*, 1H), 5.94 (*s*, 1H), 4.43-4.39 (*m*, 1H), 4.21−4.02 (*m*, 1H), 3.79 (*s*, 6H), 3.64−3.40 (*m*, 6H), 2.78−2.62 (*m*, 4H), 2.05 (*s*, 5H), 1.33−0.89 (*m*, 24H); HRESI MS: *m*/*z* Calcd for [$C_{50}H_{64}N_5O_{10}PNa$] 948.4283, found 948.4263 $[M+Na]^+$.

1,3-*O*-(4,4'-Dimethoxytrityl)propane-2-*O*-(2-cyanoethyl)-*N*,*N*-diisopropylphosphoramidite (GP) This was prepared in a similar procedure to the literature.[2] ^1H NMR (270 MHz, $CDCl_3$) δ 7.38−7.17 (*m*, 18H), 6.85−6.74 (*m*, 8H), 3.77 (*s*, 12H), 3.44−3.09 (*m*, 4H), 3.23−3.09 (*m*, 4H), 2.40 (*m*, 3H), 1.29−1.01 (*m*, 12H); HRESI MS: *m*/*z* Calcd for [$C_{54}H_{61}N_2O_8PNa$] 919.4061, found 919.4058 $[M+Na]^+$.

***O*-cyanoethyl-*O*-stearyl-*N*,*N*-diisopropylphosphoramidite (SP)** This was prepared in a similar procedure to the literature.[3] ^1H NMR (270 MHz, $CDCl_3$) δ3.88−3.80 (*m*, 2H), 3.78−3.55 (*m*, 2H), 2.64 (*t*, *J* = 6.7, 6.1, 2H), 1.57 (*br*, 34H), 1.20−1.17 (*m*, 12H), 0.88 (*t*, *J* = 6.7, 3H); HRESI MS: *m*/*z* Calcd for [$C_{27}H_{55}N_2O_2PNa$] 493.3893, found 493.3890 $[M+Na]^+$.

1) T. Kálai, J. Jekő, Z. Berente, K. Hideg, *Synthesis*. 2006, **3**, 429−446.

2) G. Oliviero, N. Borbone, J. Amato, S. D'Errico, A. Galeone, G. Piccialli, M. Varra, L. Mayol, *Biopolymer*. 2009, **91**, 466−477.

3) H. Liu, B. Kwong, D. J. Irvine, *Angew. Chem., Int. Ed*. 2011, **50**, 7052−7055.

Oligonucleotide synthesis and characterization Amidite derivatives, **TDUP**, **GP**, and **SP** were applied into solid-phase oligonucleotide synthesis protocols with an automated DNA synthesizer (Model NTS-H8:Gine World Ltd.). All oligodeoxynucleotides (ODNs) were synthesized on 1.0 μmol scale using β-cyanoethyl phosphoramidite chemistry in DMTr-ON mode. Stepwise coupling yields for modified nucleosides were all greater than 95% as determined by trityl monitoring. The synthesized ODNs were cleaved from the solid support by treatment with 28% aqueous ammonia (1 ml) for 12 hrs. at 55 °C. Complete deprotection and auto-oxidation of TEMPO moiety were accomplished by treatment with aqueous NaOH (ca. 0.5 M) for 24 h at room temperature. The solution was neutralized with cation exchange resin (H^+ form) and filtered through a 0.45 μm filter disk. Final purification of oligomers was achieved by HPLC (Nacalai tesque ODS column, COSMOCIL 5C18-ARII, or 5C4-AR300, 20 × 250 mm). Oligomers were purified under the following conditions: 5−25% MeCN in TEAA buffer (0.1 M, pH = 7.0) over 60 min; flow rate 6 ml/min; detecting at λ = 260 nm wavelength). Modified ODNs in the study were characterized by matrix-assisted laser-desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry (Table S1) by using 2 : 1 mixture of EtOH solution of 2,4,6-trihydoroxyacetophenone and water solution of ammonium citrate as matrixes.

Table S1. Data of MALDI-TOF mass spectroscopy for single strand ODNs.

	lipid-polyT$_x$				polyT$_x$			
x	out	mid	in	nat	out	mid	in	nat
Calcd. M. W.	5458	5458	5458	5320	4639	4639	4639	−
Found M. W.	5457	5457	5458	5318	4636	4638	4635	−

The formation of the double strands and their characterization The solution (< 1 mM) of TEMPO-ODNs and a complimentary strand in 10 mM phosphate buffer were mixed in a ratio of 1.0 :

1.3, warmed at 90 °C for 1 min. and then gradually cooled to room temperature. To evaluate the stability of double strands, the melting curves were obtained. The T_m values for the double strands of $polyT_{out}$, $polyT_{mid}$, $polyT_{in}$, and $polyT_{nat}$ were 48.5, 46.3, 52.0, and 50.1°C, respectively. The secondary structures of the double strands by circular dichroism (CD) spectra were confirmed to be B form.

2.

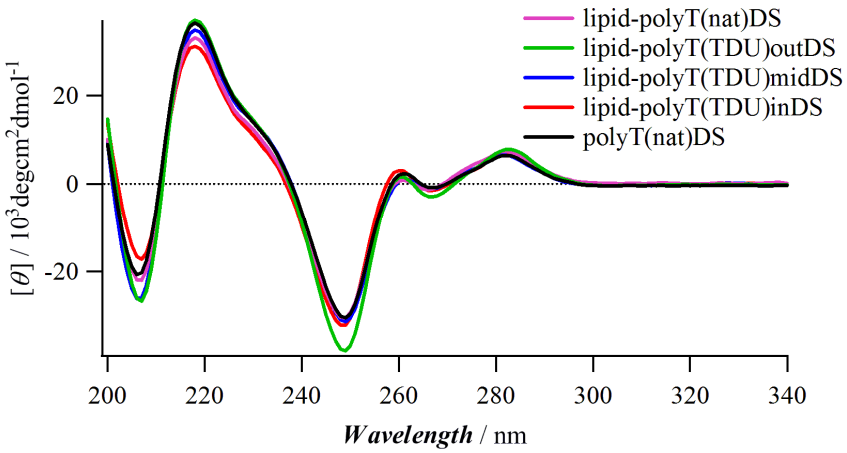


Figure S2. CD spectra of lipid-polyT(TDU)DSs, lipid-polyT(nat)DS, and polyT(nat)DS.

3.

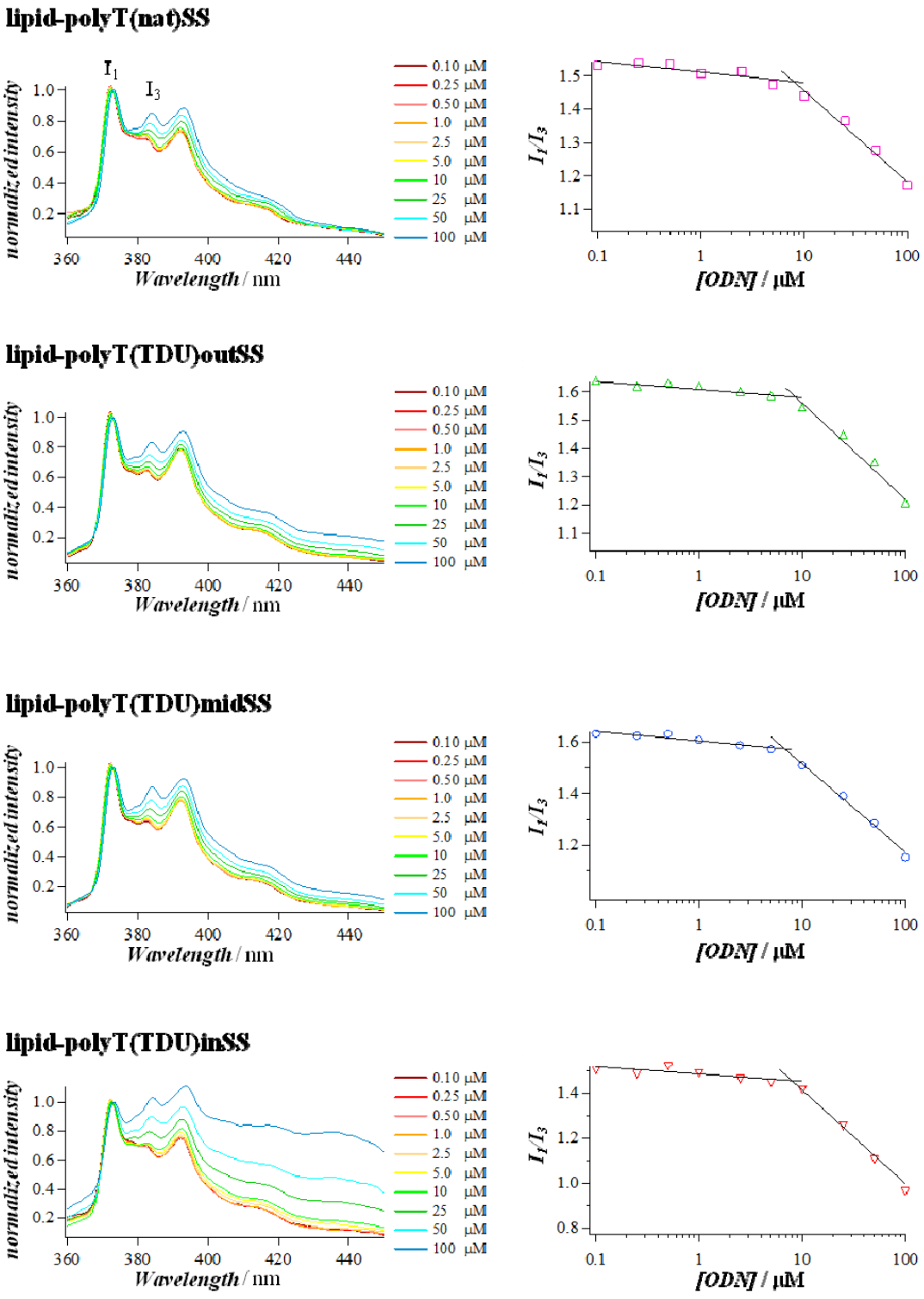


Figure S3. Emission spectra of pyrene in the presence of ODN (left) and I_1/I_3 vs. [ODN] plots (right).

4.

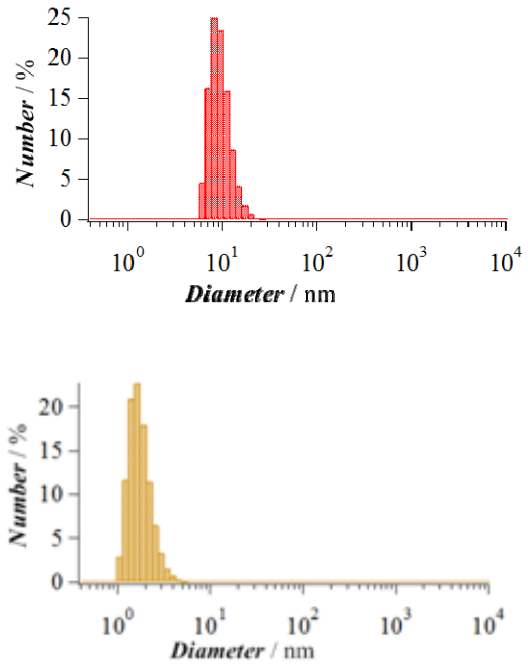


Figure S4. DLS of lipid-polyT_{in}SS (top) and polyT_{mid}SS (bottom).

5.

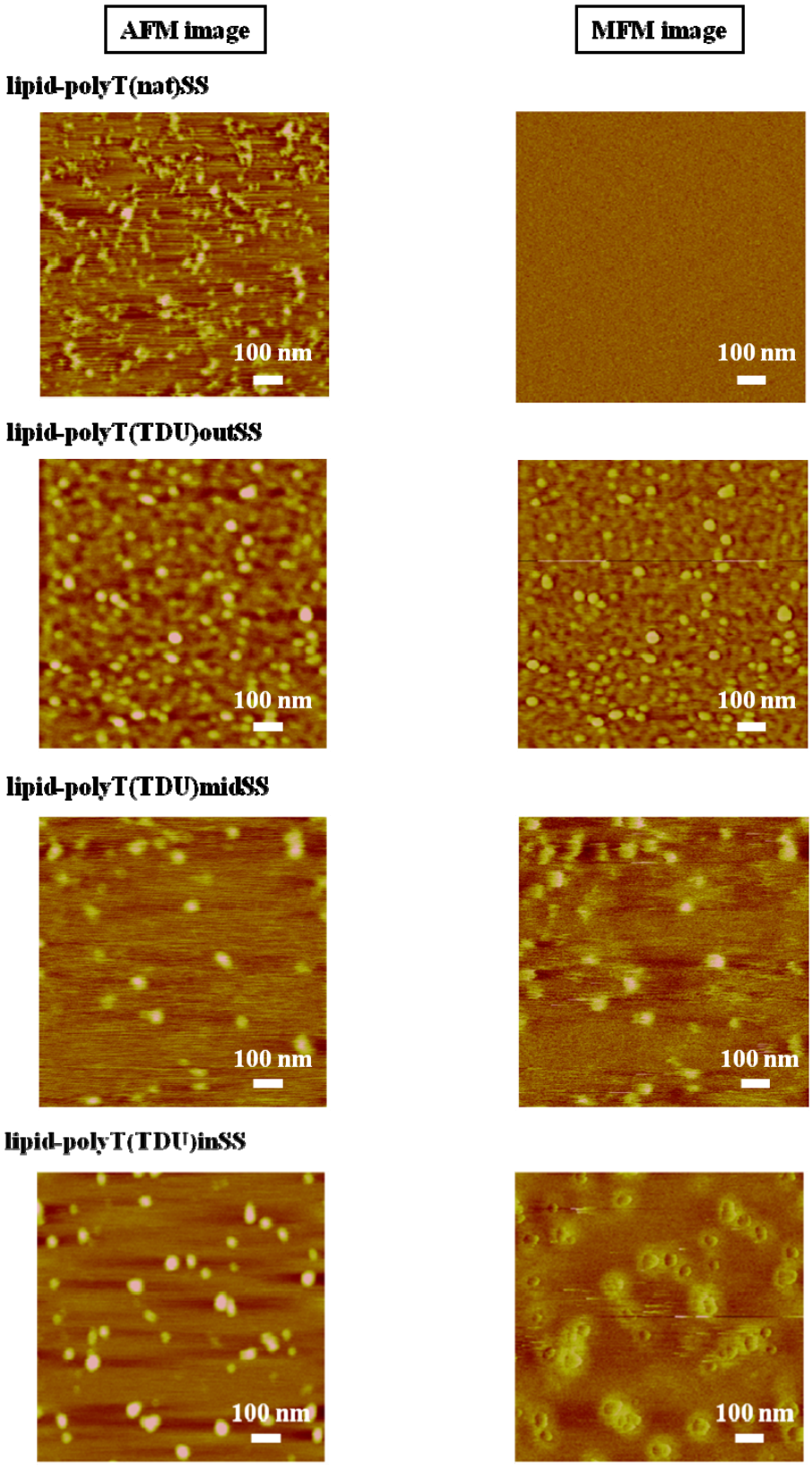


Figure S5. AFM (left) and MFM (right) images for lipid-polyT(TDU)SSs.

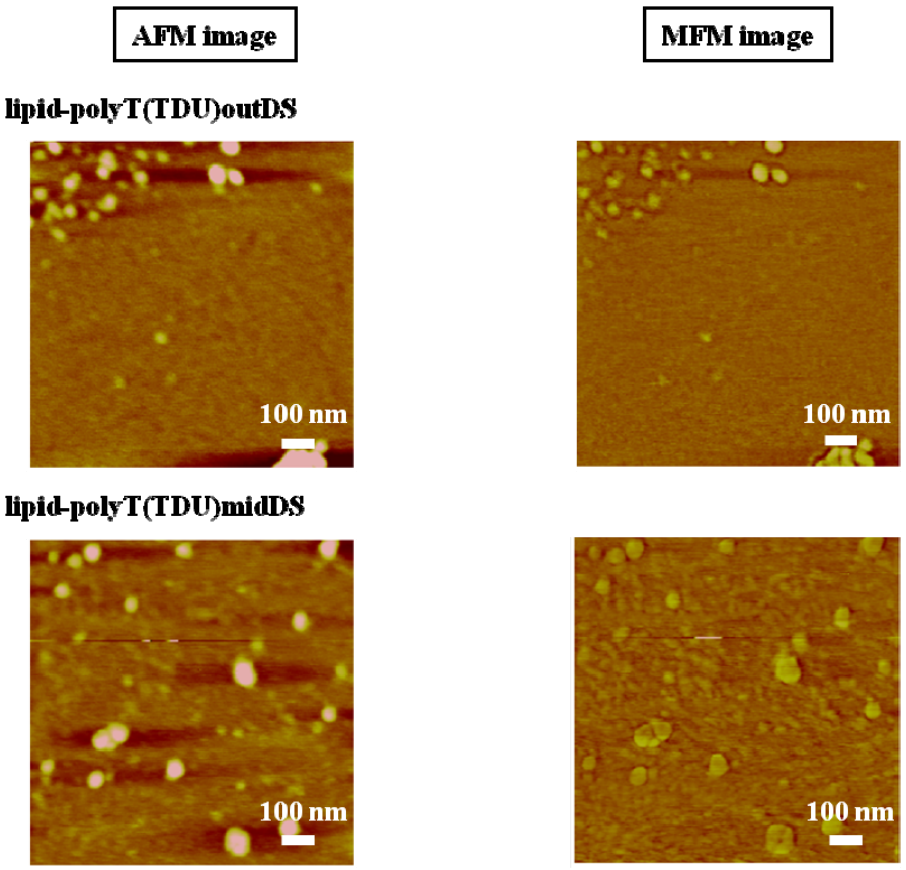


Figure S5'. AFM (left) and MFM (right) images for lipid-polyT(TDU)DSs.

6.

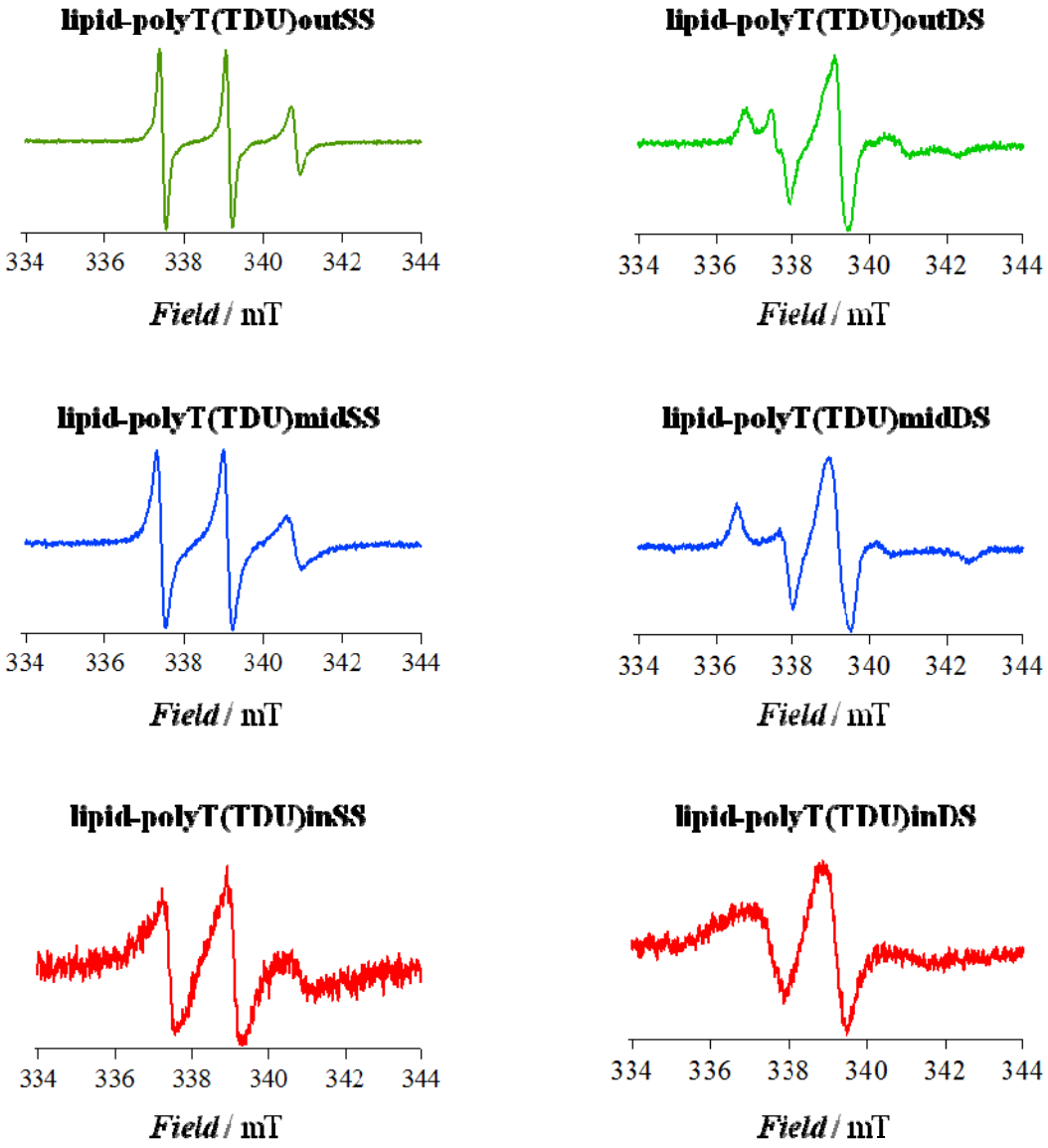


Figure S6. ESR spectra of lipid-polyT(TDU)SS (left) and lipid-polyT(TDU)DS (right).

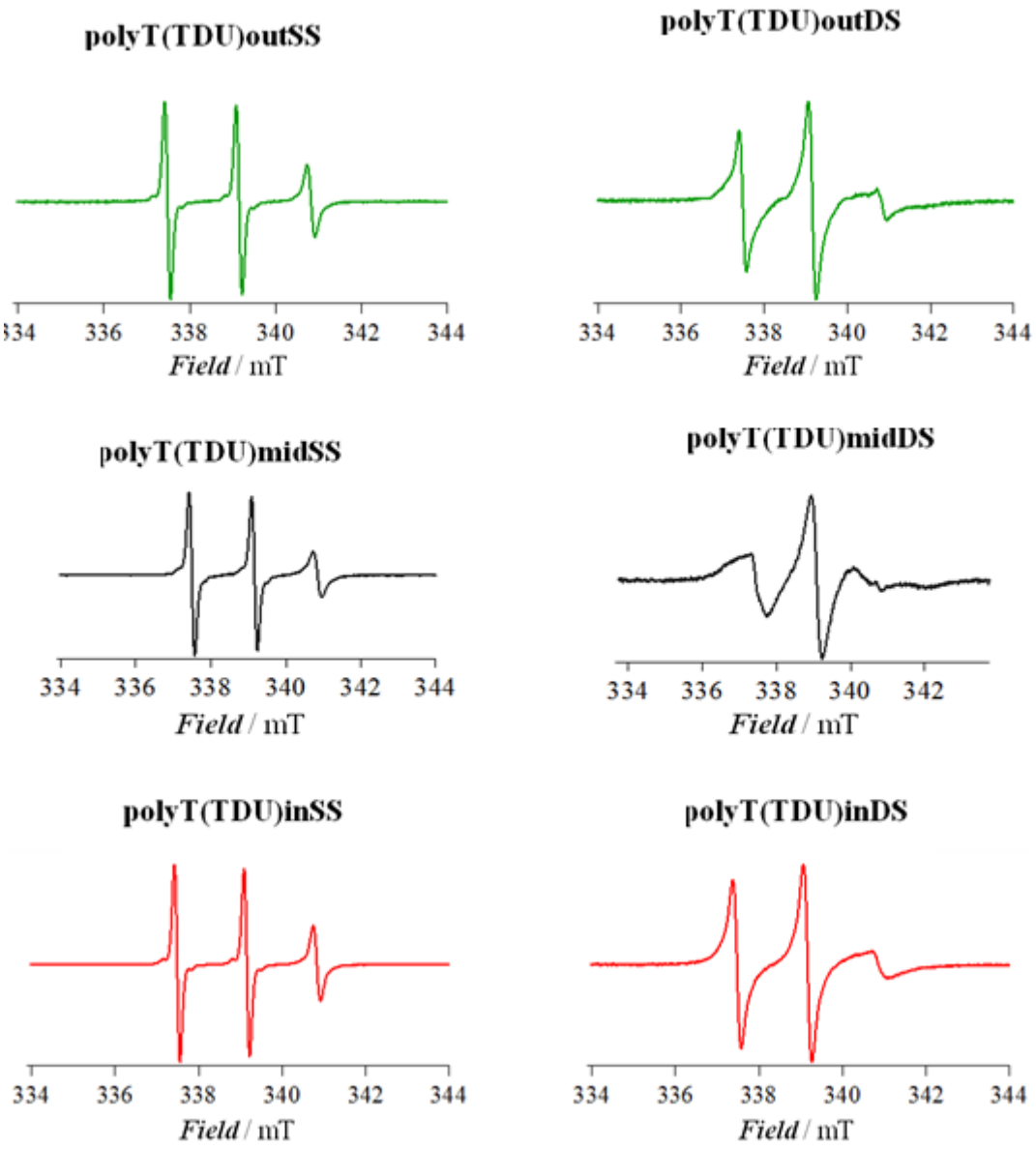


Figure S6'. ESR spectra of polyT(TDU)SS (left) and polyT(TDU)DS (right).

7.

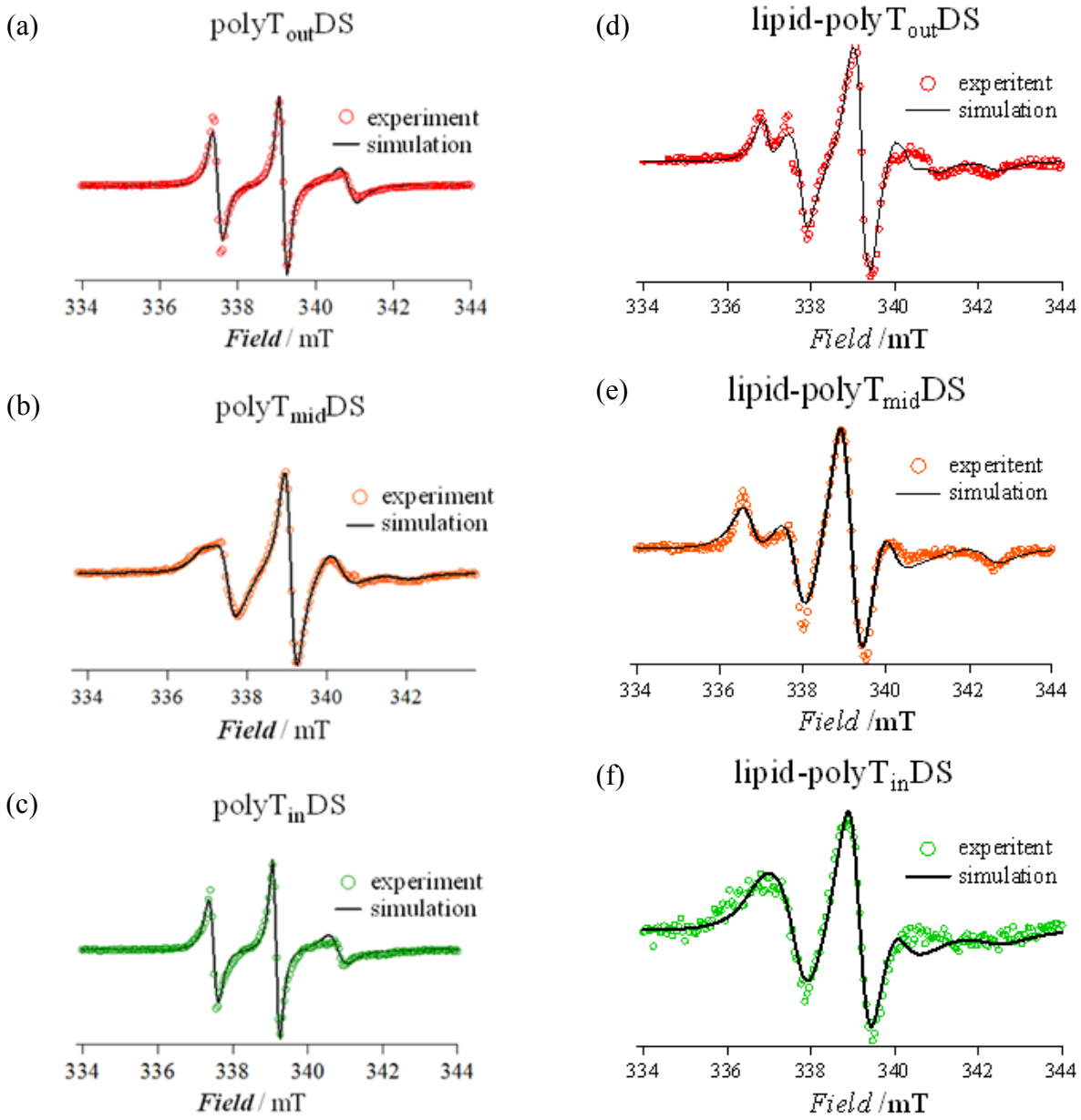


Figure S7. ESR spectra (open circle) and its simulation spectra (solid line) for polyT$_{out}$DS (a), polyT$_{mid}$DS (b), polyT$_{in}$DS (c), lipid-polyT$_{out}$DS (d), lipid-polyT$_{mid}$DS (e), and lipid-polyT$_{in}$ DS (f). Simulation were carried out in according to MOMD for (b) and (d−f), and Brownian diffusion model for (a) and (c),[1)] The obtained τ_R values are listed in Table 1.

1) a) J. J. Inbaraj, T. B. Cardon, M. Laryukhin, S. M. Grosser, G. A. Lorigan, *J. Am. Chem. Soc*. **2006**, *128*, 9549−9554. b) D. E. Budil, S. Lee, S. Saxena, J. H. Freed, *J. Magn. Reson. Ser. A*. **1996**, *120*, 155−189.

8.

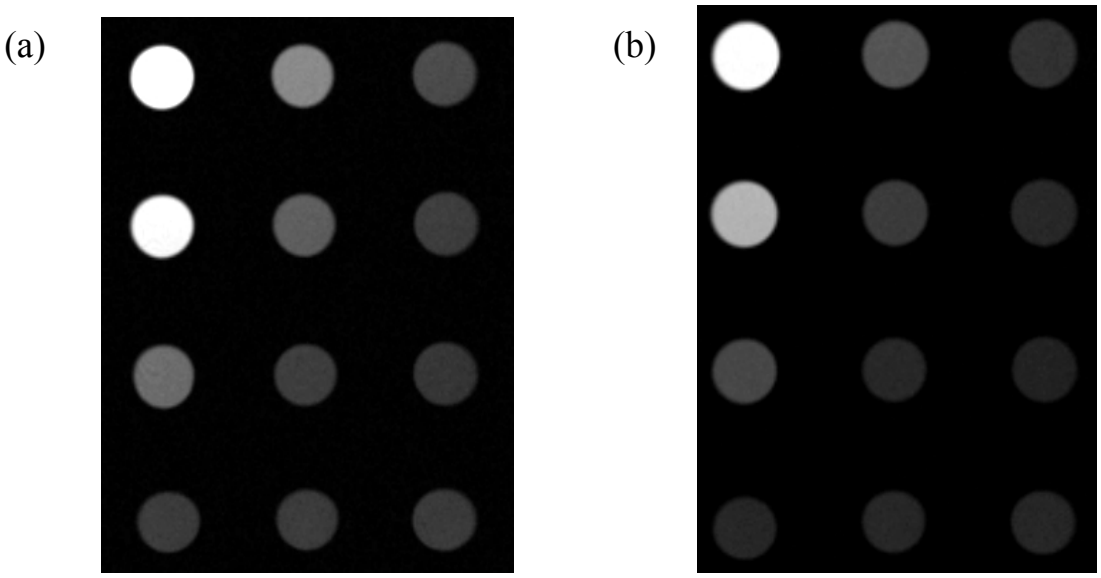


Figure S8-1. T_1-weighted images (300 MHz, 7.0 T) *in vitro* of (a) GdDTPA (left), lipid-polyT_{in}DS (middle), and TEMPO-OH (right) and (b) GdDTPA (left), lipid-polyT_{in}SS (middle), and TEMPO-OH (right). Concentrations were 1.0, 0.5, 0.1, and 0.0 mM from the top to the down.

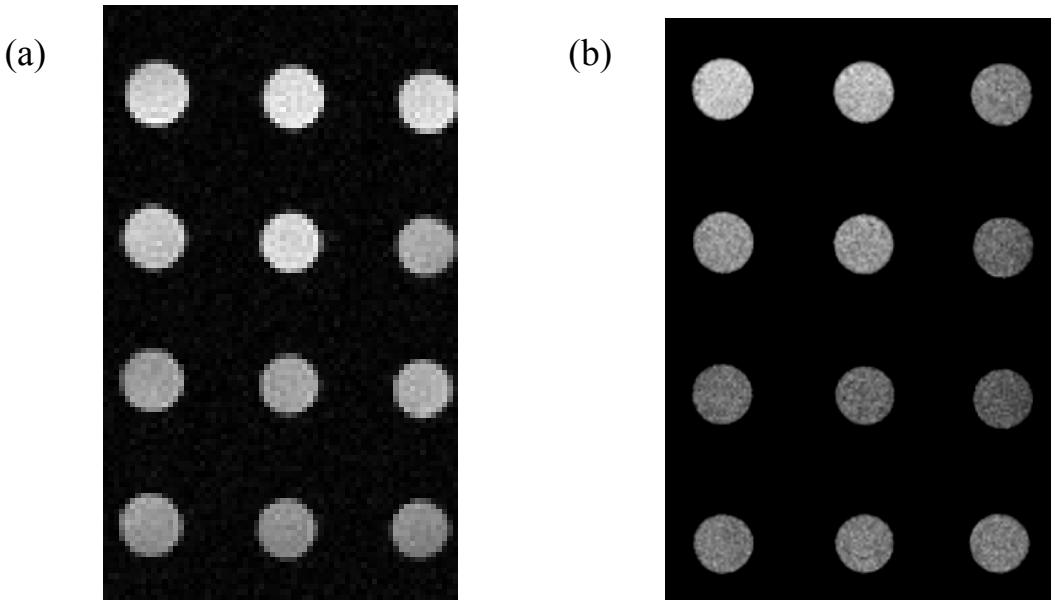


Figure S8-2. T_1-weighted images *in vitro* of lipid-polyT_{mid}DS (left), lipid-polyT_{out}DS (middle), and TEMPO-OH (right) in 42 MHz, 1.0 T (a) and 300 MHz, 7.0 T (b). Concentrations were 0.5, 0.3, 0.1, and 0.0 mM from the top to the down.

(a) (b)

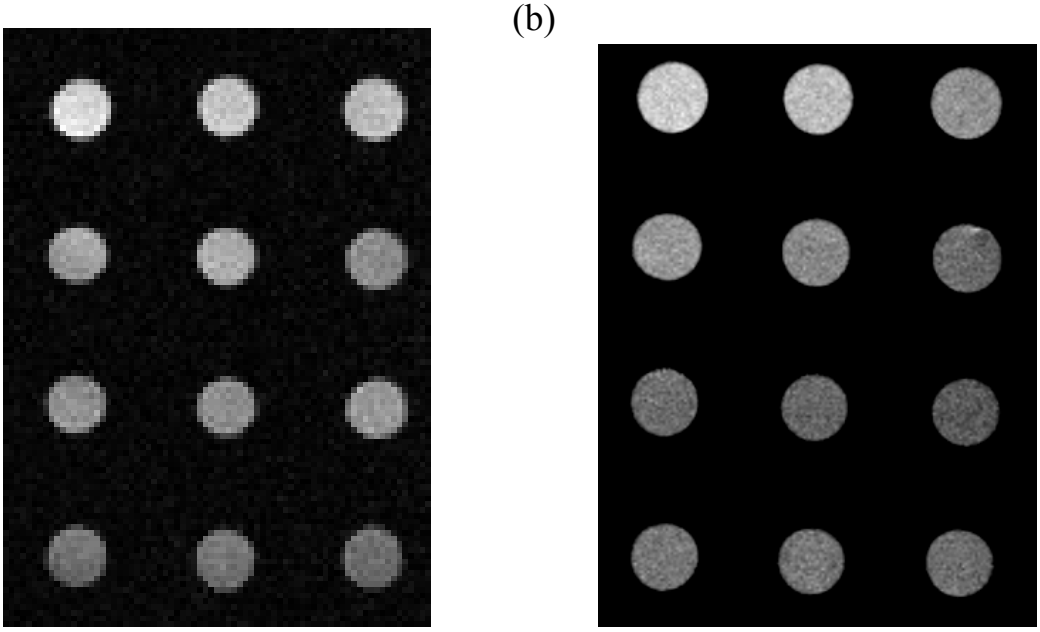


Figure S8-3. T_1-weighted images *in vitro* of polyT_{mid}DS (left), polyT_{mid}SS (middle), and TEMPO-OH (right) in 42 MHz, 1.0 T (a) and 300 MHz, 7.0 T (b). Concentrations were 0.5, 0.3, 0.1, and 0.0 mM from the top to the down.