Electronic Supplementary Material (ESI) for Soft Matter.

Electric Supplementary Information for

Photoinduced binding of malachite green copolymer to parallel G-quadruplex DNA

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Molecular weight and molar fraction data of PVAMG

Table S1 Molecular weight and molar fraction data of PVAMG

Copolymer	M_w	M_w/M_n	x
PVAMG1	8.2×10^4	1.79	8.7×10^{-4}
PVAMG2	6.8×10^4	1.84	8.3×10^{-4}

The average molar mass (M_n) and weight-average molar mass (M_w) of PVAMGs are determined by gel permeation chromatography using poly(methyl methacrylate) calibration standards. The molar fraction of the malachite green unit (x) was estimated by the NMR spectra of PVAMGs.

Backward reaction of PVAMG

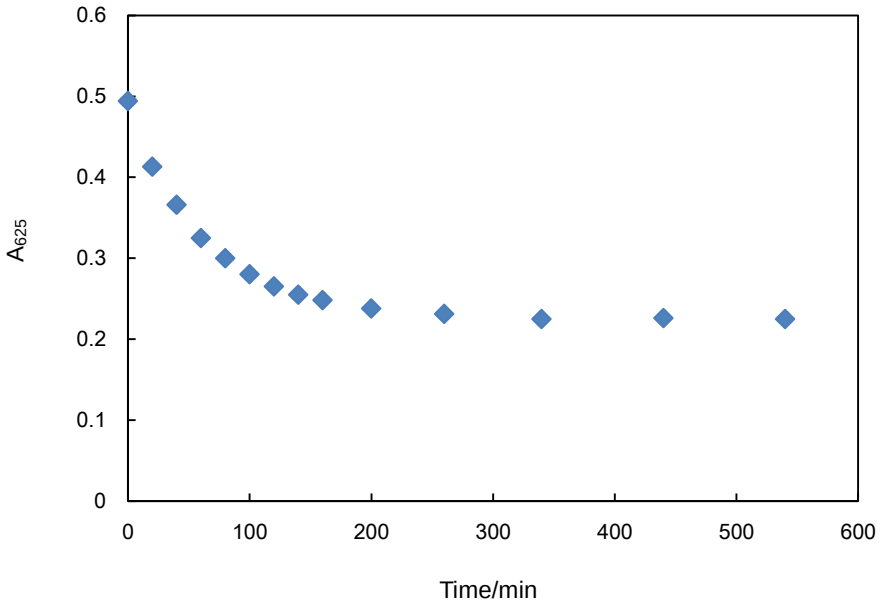

Figure S1 Time dependence of absorbance at 625 nm (A_{625}) for PVAMG2 (0.5g/L) after irradiation for 25 min in Tris-HCl buffer (10 mM, pH 7.4) containing 1 mM EDTA and 100 mM KCl. The solution was kept at 25°C.

CD spectra of G-quadruplexes

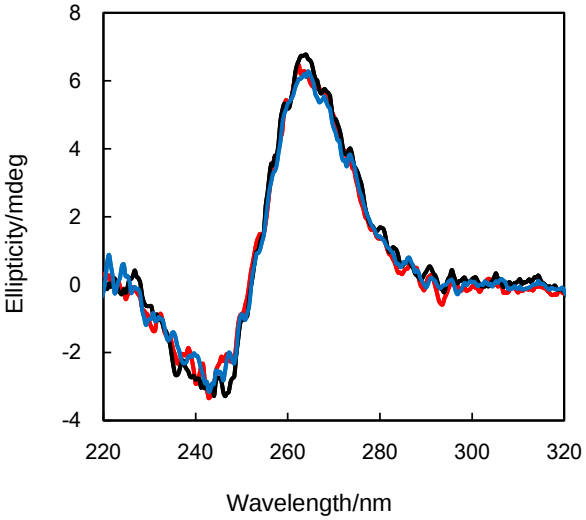

Figure S2 CD spectra of c-MYC22 (10 μM) in Tris-HCl buffer (10 mM, pH 7.4) containing 1 mM EDTA and 100 mM KCl. The concentration of coexisting MG^+ of PVAMG1 was 0 (black), 34 (red), and 85 (blue) μM. A positive peak at 264 nm and a negative peak at 244 nm are consistent with parallel topology.[1,2]

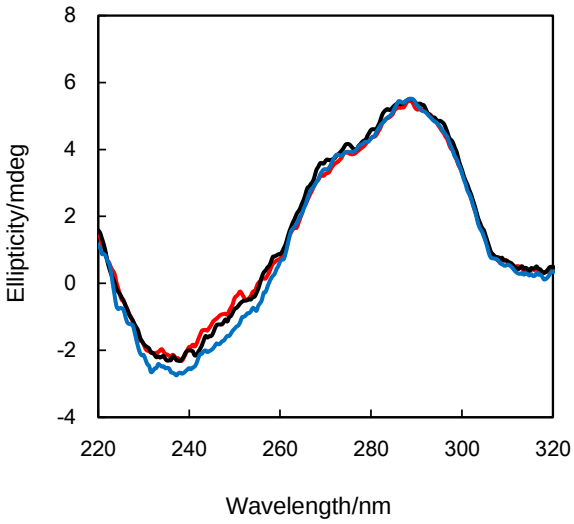

Figure S3 CD spectra of Telo24 (10 μM) in Tris-HCl buffer (10 mM, pH 7.4) containing 1 mM EDTA and 100 mM KCl. The concentration of coexisting MG^+ of PVAMG2 was 0 (black), 66 (red), and 135 (blue) μM. A large positive peak at 290 nm, indicates contribution from antiparallel structure. The spectra also show a positive shoulder at 275 nm, a small hump at 255 nm, and a negative peak at 238 nm, indicating contributions from parallel topology[3,4].

(1) E. Hatzakis, K. Okamoto, D. Yang, *Biochemistry* **2010**, *49*, 9152-9160.

(2) V. Dapić, V. Abdomerović, R. Marrington, J. Peberdy, A. Rodger, J. O. Trent, P. J. Bates *Nucleic Acids Res.* **2003**, *15*, 2097-2107

(3) S. D. Verma, N. Pal, M. K. Singh, H. Shweta, M. F. Khan, S. Sen, *Anal. Chem.* **2012**, *84*, 7218‑7226.

(4) X. Zhang, J. Xiang, M. Tian, Q. Yang, H. Sun, S. Yang, Y. Tang, *J. Phys. Chem. B* **2009**, *113*, 7662‑7667.

Estimation of binding constant

The concentrations of PVAMGs were expressed as MG^+. The fluorescence intensity at 640 nm of PVAMG or MG oxalate was obtained in the solution containing various amounts of oligonucleotides when the concentration of MG^+ was maintained at a constant of 2 μM. The binding constant is estimated from the change in the fluorescence using Benesi-Hildebrand equation.[5]

$$1/\Delta F = 1/(K_a \cdot \Delta F_0)[DNA] + 1/\Delta F_0$$

where ΔF is florescence intensity change, K_a is the binding constant, and ΔF_0 is maximum florescence intensity change. We have plotted 1/ΔF vs 1/[DNA] in the DNA concentration range from 2 to 20 μM. The double reciprocal plot is linear and the slope gives $1/(K_a \cdot \Delta F_0)$. Figure S4 shows plots for the sample of PVAMGs and G-quadruplexes.

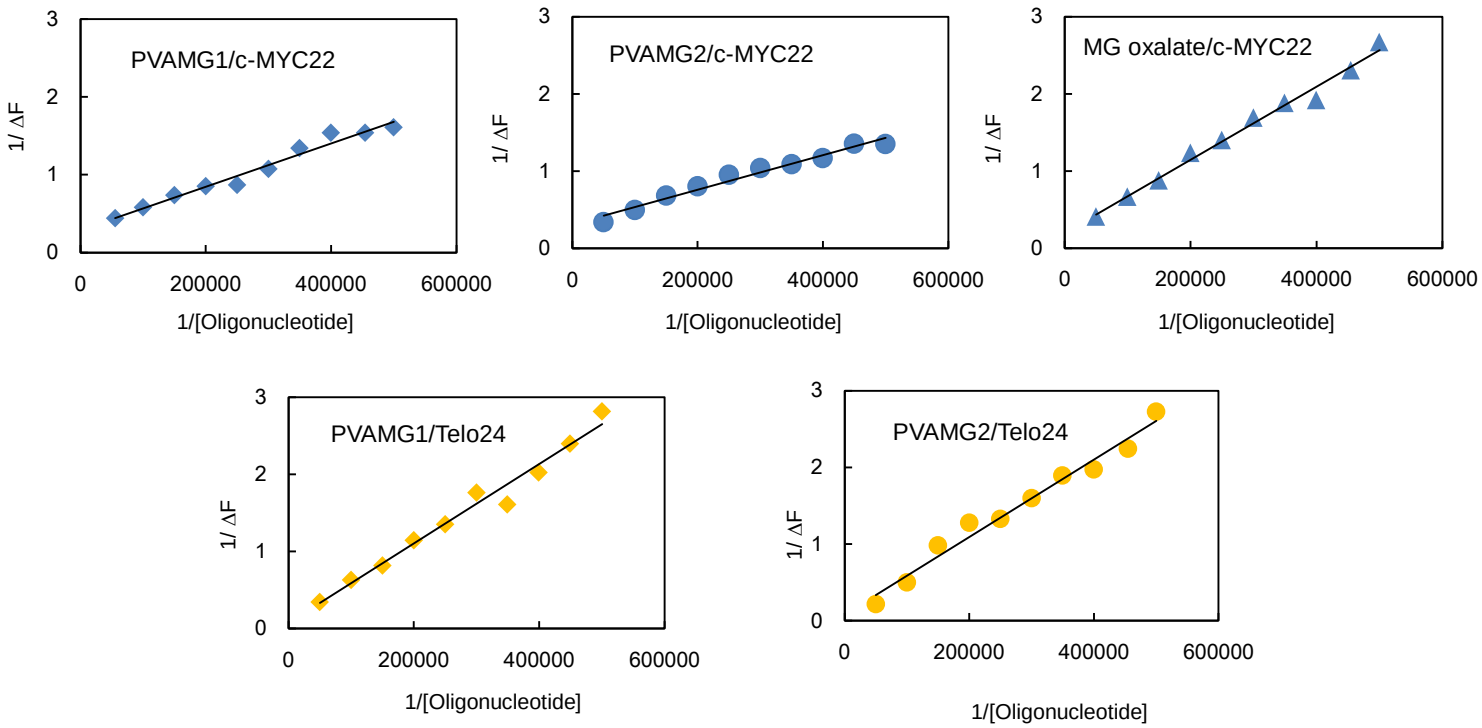

Figure S4. Benesi-Hildebrand plots of MG^+ (2 μM) and G-quadruplex. The extrapolation of the ordinate corresponds to $1/\Delta F_0$ and the slope corresponds to $1/(K_a \cdot \Delta F_0)$. The fluorescence intensity was calibrated with the fluorescence of 3.0 μM malachite green oxalate in acetate buffer solution (0.1 M, pH 4.0) containing 1.0 gL^{-1} of poly(vinyl alcohol).

(5) H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* **1949**, *71*, 2703-2707

Estimation of binding ratio

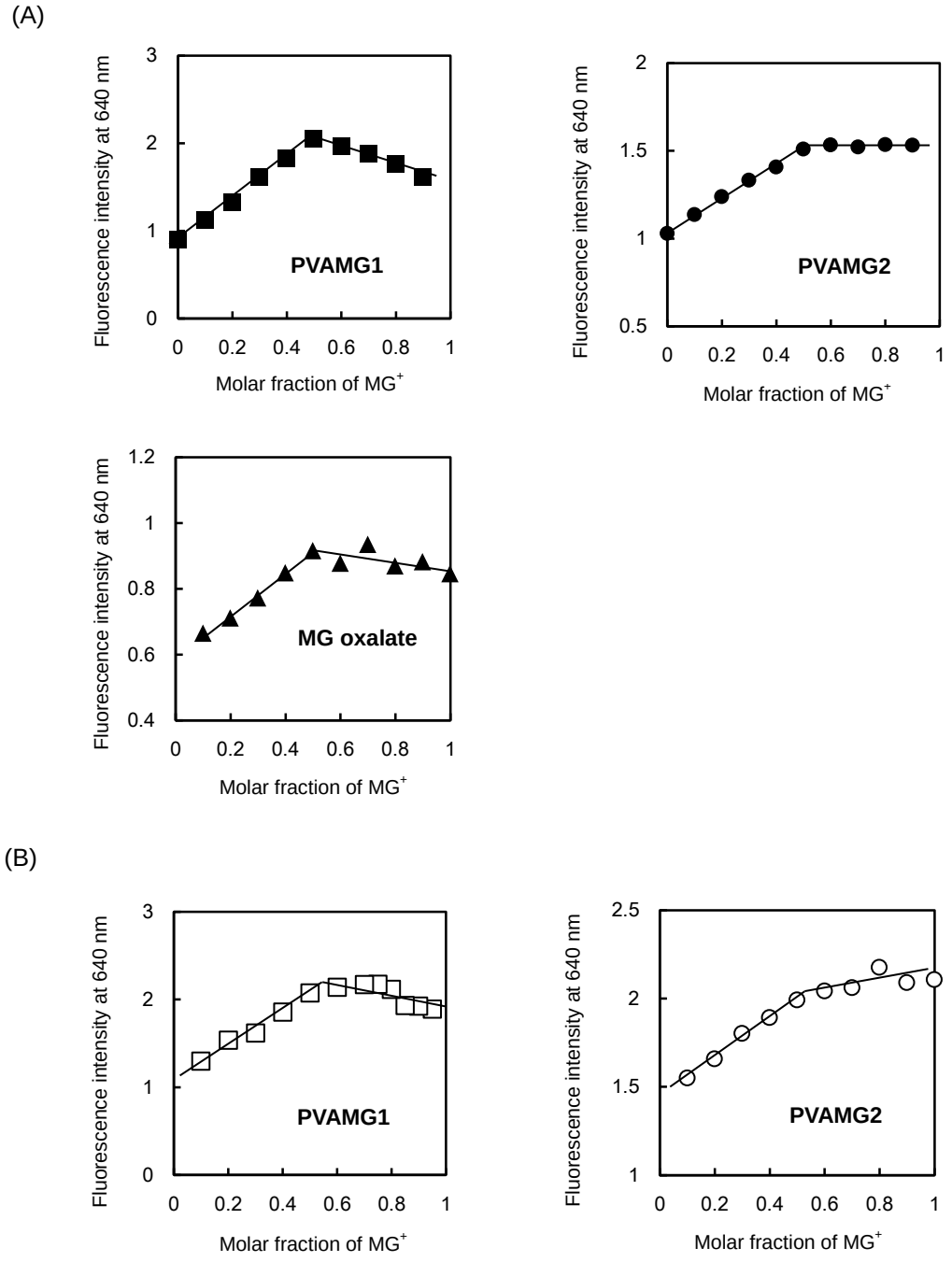

Figure S5. Job plots for MG^+ binding to c-MYC22 G-quadruplex (A) and Telo24 G-quadruplex (B). The total concentration of MG^+ and G-quadruplex was kept at 4 μM. The fluorescence intensity was obtained by the excitation at 590nm and calibrated with the fluorescence of 3.0 μM malachite green oxalate in acetate buffer solution (0.1 M, pH 4.0) containing 1.0 gL^{-1} of poly(vinyl alcohol).

CD spectra of PVAMGs

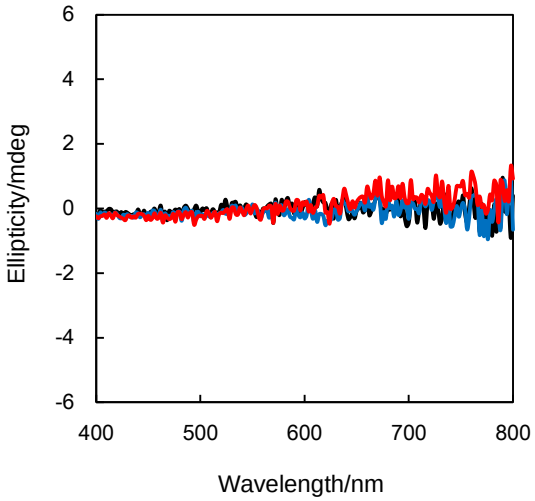

Figure S6 CD spectra of irradiated PVAMG2 (5 μM) binding to c-MYC22 G-quadruplex. The concentration of c-MYC22 was 0 (black), 5 (blue) and 10 (red) μM. 1-cm cell was used.

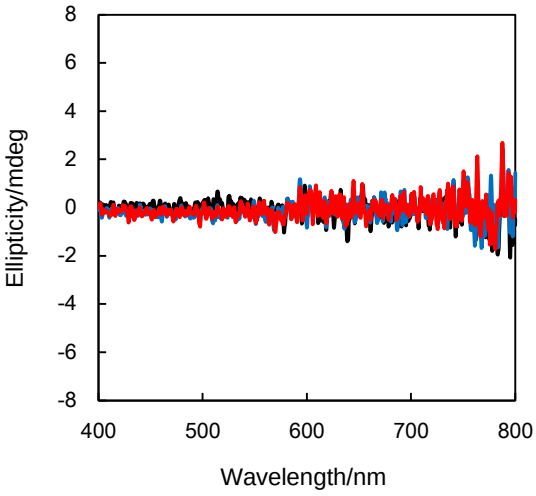

Figure S7 CD spectra of irradiated PVAMG1 (8 μM) binding to Telo24 G-quadruplex. The concentration of Telo24 was 0 (black), 8 (blue), and 16 (red) μM. 1-cm cell was used.

Temperature dependence of absorbance of PVAMG

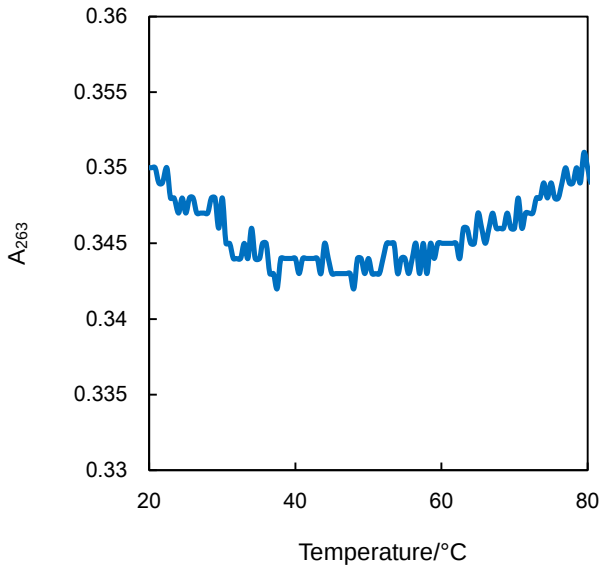

Figure S8 Temperature dependence of absorbance at 263 nm (A_{263}) for PVAMG2 (10 μM). The PVAMG2 solution was prepared by using a buffer containing KCl (1 mM) and LiCl (99 mM).

Polymerase stop assay in the presence of MG oxalate

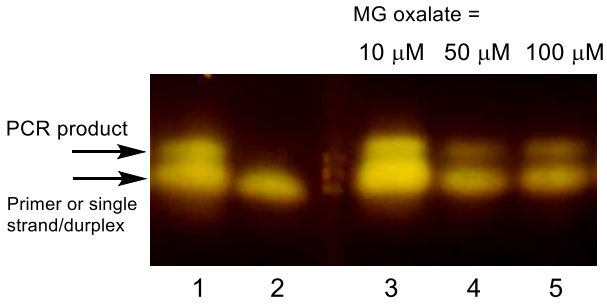

Figure S9 Effect of MG oxalate binding in polymerase stop assay with G-quadruplex forming c-MYC27 oligomer. (Lane 1) Positive control. (Lane 2) Negative control. 10 μM (Lane 3), 50 μM (Lane 4), and 100 μM (Lane 5), respectively of MG oxalate were added to c-MYC oligomer (5 μM).

Environment of MG^+ in complexing with G-quadruplex

The wavelength at maximum absorbance (λ_{max}) of MG^+ were plotted in Figure S10. The peak of MG^+ was hardly changed by the interaction with Telo24 quadruplex, while a red shift was observed by c-MYC22 quadruplex. The peak of the triphenylmethane dye in the visible region is red-shifted in a solvent with a low dielectric constant.[6,7] In the other words, MG^+ binds to c-MYC22 G-quadruplex in the environment more hydrophobic than that in the complex of MG^+ with Telo24 G-quadruplex.

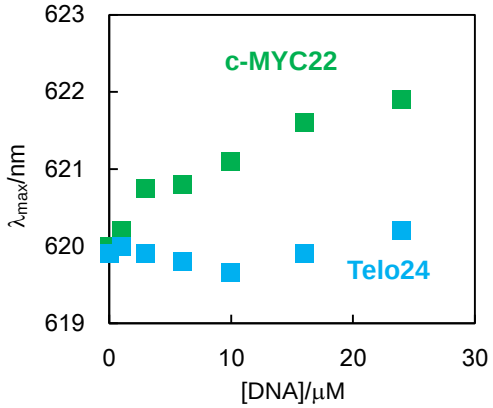

Figure S10. Changes in wavelength at maximum absorbance (λ_{max}) of MG^+ of PVAMG1 (5 μM).

(6) K. K. Karukstis, A. V. Gulledge, *Anal. Chem.* **1998**, *70*, 4212–4217
(7) R. M. Uda, K. Kimura, *Colloid Polym. Sci.* **2007**, *285*, 699–704.