Supporting Information

Proton Transfer of Guanine Radical Cations Studied by Time-resolved Resonance Raman Spectroscopy Combined with Pulse Radiolysis

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Experimental Section

The 2′-deoxyguanosine-5′-monophosphate (5′-dGMP) was purchased from Sigma-Aldrich and used without further purification. Ammonium persulfate and *tert*-butyl alcohol was purchased from Wako Pure Chemical Industries, Ltd. and Nacalai Tesque, respectively, and used without purification.

Pulse radiolysis. Pulse radiolysis experiments were performed using an 8-ns electron (27 MeV, 11 A, 8 ns, 0.8 kGy per pulse) generated by a linear accelerator at Osaka University. Aqueous solutions of 50 mM 5′-dGMP containing 0.1 M ammonium persulfate ($(NH_4)_2S_2O_8$), 100 mM sodium phosphate buffer, and 0.1 M *tert*-butyl alcohol (for scavenging OH radicals) were saturated with Ar gas by bubbling for 15 min at room temperature before radiolysis. The probe light was obtained from a pulsed 450-W Xe arc lamp (Ushio, UXL-451−0), which was operated by a large current pulsed power supply that was synchronized with an 8-ns electron pulse. The probe light was passed through an iris with a diameter of 0.3 cm and sent into the sample solution at an intersection perpendicular to the 8-ns electron pulse. The kinetic measurements were performed using a nanosecond photoreaction analyzer system (Unisoku, TSP-1000). The probe light passing through the sample was focused on the entrance slit of a monochromator (Unisoku, MD200) and detected with a photomultiplier tube (Hamamatsu Photonics, R2949). The transient absorption spectra were measured using a photodiode array (Hamamatsu Photonics, S3904-1024F) with a gated image intensifier (Hamamatsu Photonics, C2925−01) as a detector.

TR^3 spectroscopy combined with pulse radiolysis: All 5′-dGMP (50 mM) solutions were purged with Ar gas during the TR^3 measurements. The Raman experiments were performed by the flow of sample solution through a quartz capillary tube at a rate sufficient to ensure that each electron beam and laser flash encounter a fresh sample volume. When we need accumulation to improve the signal-to-noise ratio, the sample was frequently replaced by a

fresh sample. The TR^3 spectra of 5′-dGMP after an 8-ns electron pulse were obtained by photoexcitation with a 532-nm flash, which is the second harmonic from a nanosecond Q-switched Nd:YAG laser (5 ns fwhm, Brilliant, Quantel; Les Ulis, France). The laser excitation light is synchronized with an 8-ns electron pulse. The sample solution was passed through a quartz capillary tube at a slow rate sufficient to ensure that each laser flash encountered a fresh volume of the sample. The TR^3 spectra were collected using a monochromator (Acton, SP2500i; Trenton, NJ, USA) equipped with a charge-coupled device (CCD) camera (Princeton Instruments, PI-MAX3; Trenton, NJ, USA).

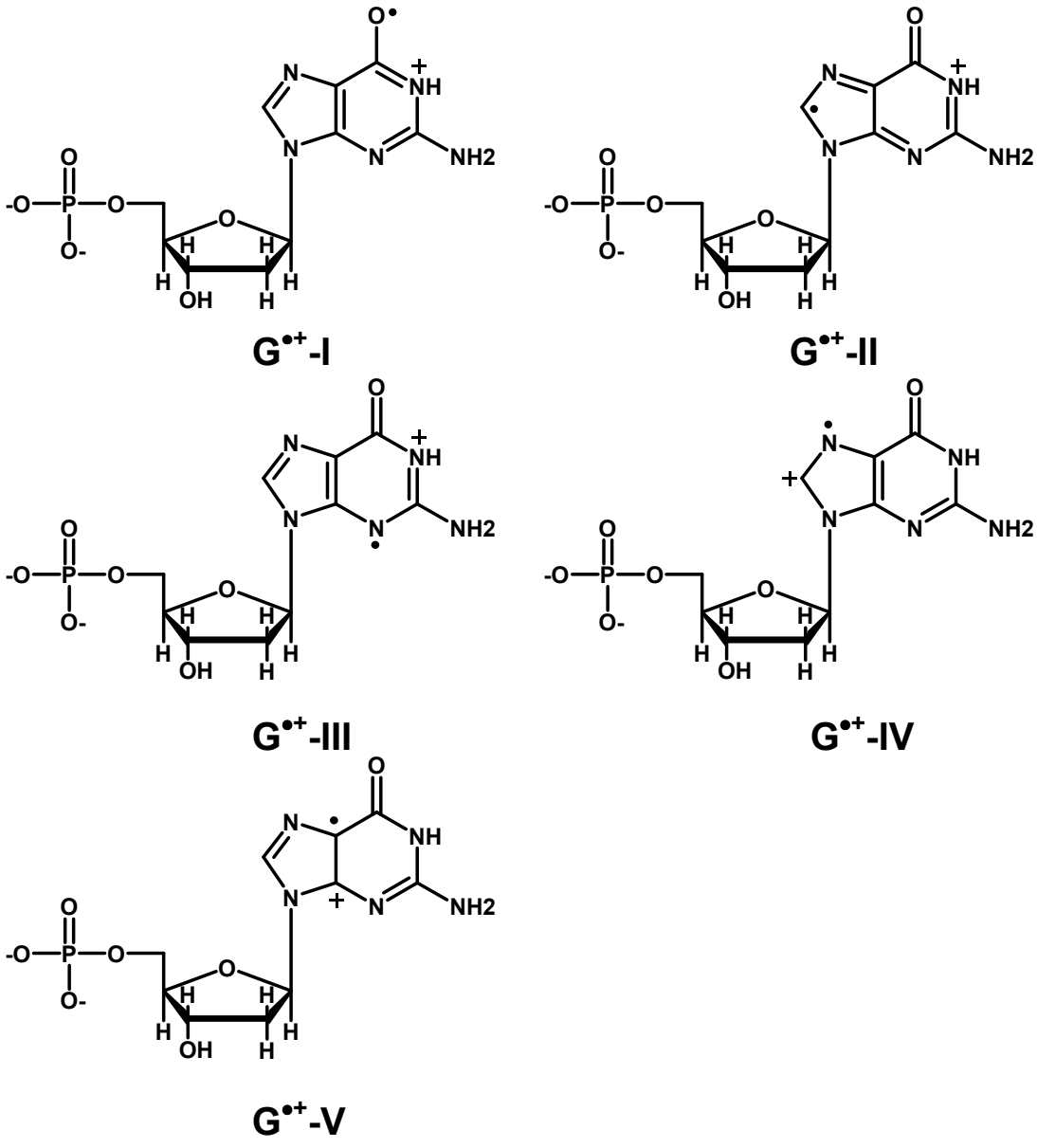

Figure S1. Proposed Structures of $G^{\bullet+}$.

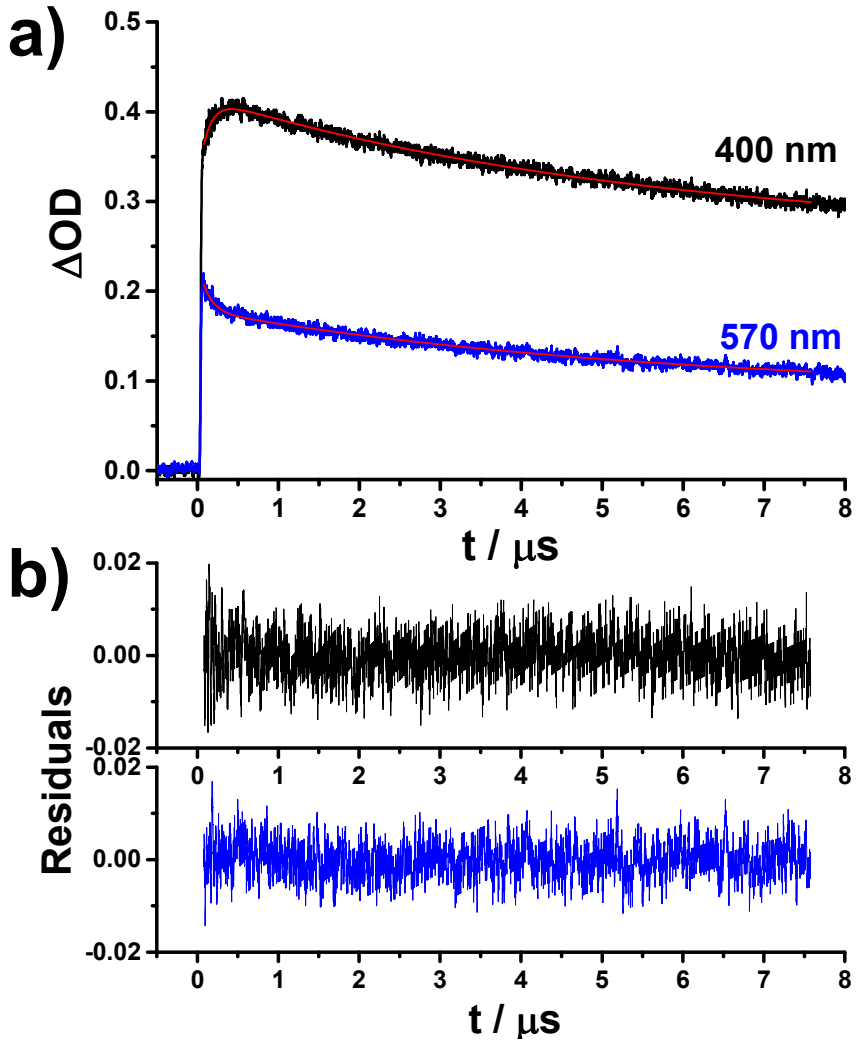

Figure S2. a) Absorbance changes at 400 and 570 nm after pulse radiolysis of 5′-dGMP in 100 mM Na phosphate buffer (pH 7.4) containing 0.1 M ammonium persulfate ($(NH_4)_2S_2O_8$) and 0.1 M *tert*-butyl alcohol. b) Residuals of global fitting results.