Supporting Information

Chemical redox-induced chiroptical switching of supramolecular assemblies of viologens

Yutaka Kuwahara,[a,b*] Mio Ito,[a] Makoto Takafuji,[a,b] Hirotaka Ihara,[a,c] Naoya Ryu,[d] and Tomoyasu Mani[e]

[a] *Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan. E-mail: kuwahara@kumamoto-u.ac.jp*

[b] *International Research Organization for Advanced Science and Technology (IROAST), Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan.*

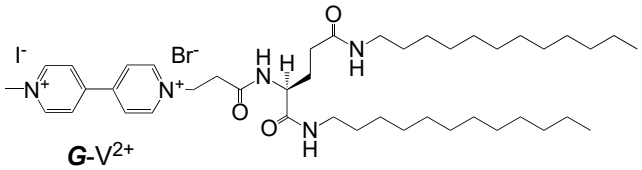
[c] *National Institute of Technology, Okinawa College, 905 Henoko, Nago, Okinawa 905-2192, Japan.*

[d] *Materials Development Department, Kumamoto Industrial Research Institute 3-11-38 Higashimachi, Higashi-ku Kumamoto 862-0901, Japan.*

[e] *Department of Chemistry, University of Connecticut, 55 N. Eagleville Rd, Storrs, CT 06269-3060, United States.*

NMR spectroscopy of $_L$-glutamic acid derivatives, ***G***-V^{2+}.

The ^1H and ^{13}C NMR spectra of ***G***-V^{2+} were measured in DMSO-d_6 at 25 °C (Figure S3). The ***G***-V^{2+} was identified from a result of the high resolution ^1H-NMR spectrum (Figure S3a). However, we only obtained a ^{13}C NMR spectrum with low resolution in DMSO-d_6, as shown in Figure S3b, due to the low concentration of ***G***-V^{2+} ([***G***-V^{2+}] = 1.1 mM). A D_2O solution of higher concentration (3.8 mM) of ***G***-V^{2+} was prepared because we were unable to prepare a DMSO solution with a concentration higher than 1.1 mM owing to the poor solubility of the ***G***-V^{2+} for DMSO. For the ^1H NMR spectra of the D_2O solution ([***G***-V^{2+}] = 3.8 mM) at 25 ºC, peak-broadening and decrease in the number of peaks were observed due to aggregation of the ***G***-V^{2+} and hydrogen bond formation on the amide groups. For ^{13}C NMR spectra, no peak was observed at 25 and 70 ºC because aggregation and partial gelation of the ***G***-V^{2+} was occurred in the D_2O solution. Therefore, ***G***-V^{2+} could not be characterized by the ^{13}C NMR spectra in this study.



G-V^{2+}

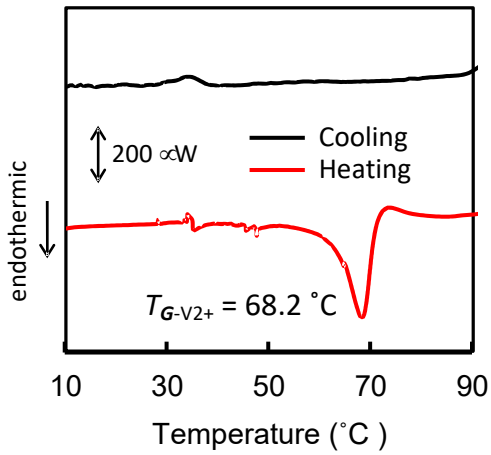
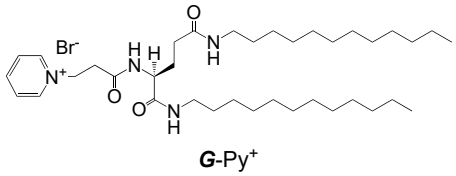


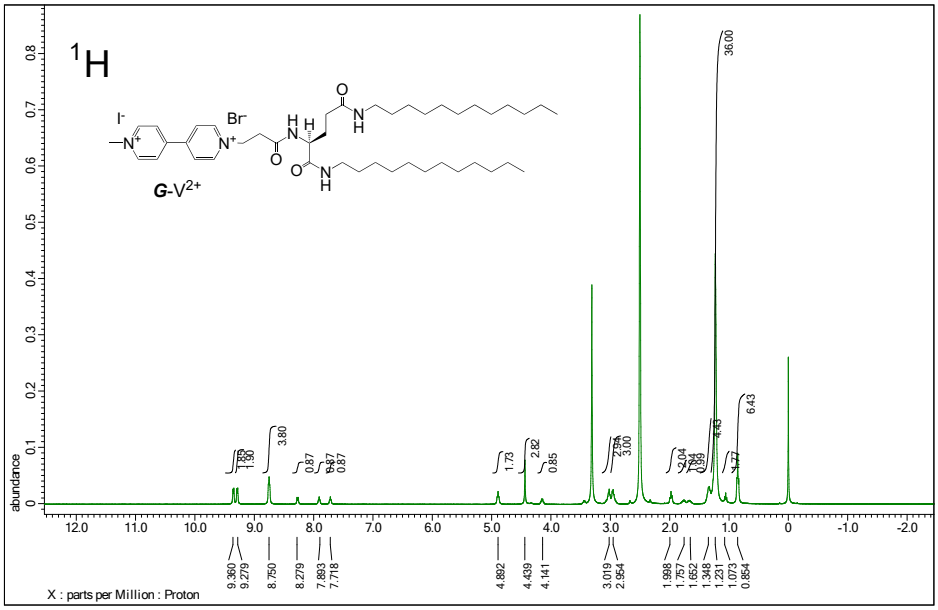
Figure S1. DSC thermograms of an aqueous solution of ***G***-V^{2+} (20 mM). The heating rate was 2 °C/ min. $T_{G\text{-}V2+}$ is a phase-transition temperature of the aqueous ***G***-V^{2+} solution.



G-Py^+

Figure S2. Structure of mono-pyridinium- (N-ethyl pyridinium-) substituted glutamide (***G***-Py^+).

(a)



(b)

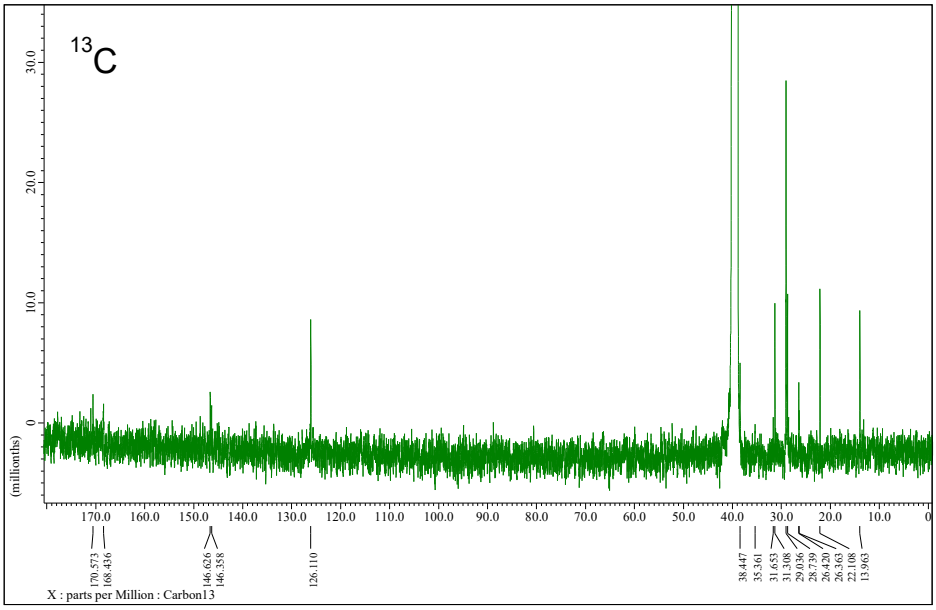


Figure S3. ^{1}H-NMR (a, 400 MHz) and ^{13}C-NMR (b, 100 MHz) spectra of ***G***-V^{2+} (DMSO-d_6, TMS, 25 °C).

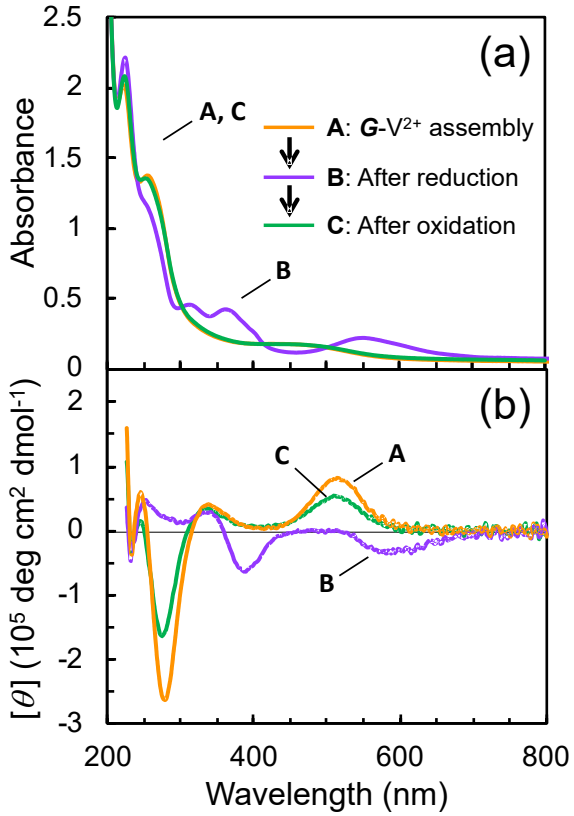


Figure S4. (a) UV-vis absorption and (b) CD spectra of an aqueous ***G***-V^{2+} solution (0.5 mM) before reduction (line A), after reduction via sodium dithionite (0.5 mM) under an Ar atmosphere (line B), and after subsequent oxidation via air exposure at 10 °C (line C). The cell path length was 1 mm.

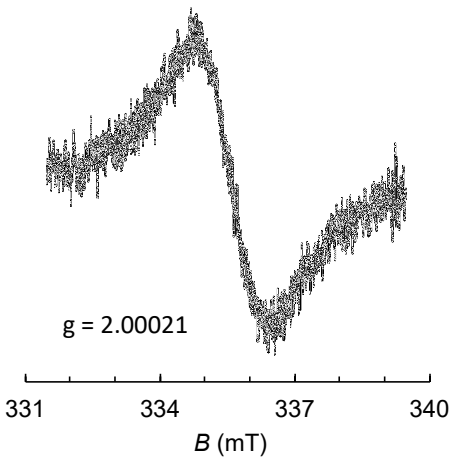
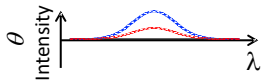
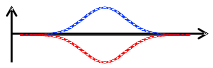
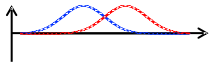
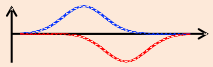
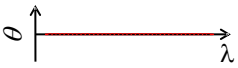


Figure S5. ESR spectrum of an aqueous ***G***-V^{2+} solution (0.5 mM) chemically reduced using sodium dithionite (0.6 mM) at 20 °C. Experimental parameters: modulation frequency = 100 kHz; modulation amplitude = 0.05 mT; sweep time = 900 s; time constant = 0.3 s; center field = 336.000 mT; sweep width = 1.0 mT; and microwave power = 2.5 mW. The *g*–factor (dimensionless magnetic moment) was calculated using a MgO:Mn^{2+} marker.

Table S1. Classification of electro-responsive chiroptical switching (ECSw) behaviors (types I–IV) with comparison to electrochromic behavior and spectral responses in the visible region.

Type	Color change[a]	Chiroptical changes[b]			Previous works [1-18]
		Sign	Intensity	Spectral response[c]	
I	N[d]	N	Y[e]		Ref. 1-9
II	N	**Y**	Y/N		Ref. 10,11
III	**Y**	N	Y/N		Ref. 12–16
IV	**Y**	**Y**	Y		Ref. 6,17,18
Electro-chromism	Y	No signal			

a: Light absorption in the visible region; b: Electronic circular dichroism (CD) or circularly polarized luminescence (CPL) spectroscopy; c: Original (blue) and response (red) CD or CPL spectra in the visible region; λ is wavelength, θ is ellipticity. d: No change. e: Change.

References

1. J.-i. Nishida, T. Suzuki, M. Ohkita and T. Tsuji, *Angew. Chem. Int. Ed.*, 2001, **40**, 3251-3254.
2. Z. Y. Wang, E. K. Todd, X. S. Meng and J. P. Gao, *J. Am. Chem. Soc.*, 2005, **127**, 11552-11553.
3. T. Suzuki, R. Yamamoto, H. Higuchi, E. Hirota, M. Ohkita and T. Tsuji, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1937-1942.
4. H. Higuchi, E. Ohta, H. Kawai, K. Fujiwara, T. Tsuji and T. Suzuki, *J. Org. Chem.*, 2003, **68**, 6605-6610.
5. A. E. Holmes, D. Das and J. W. Canary, *J. Am. Chem. Soc.*, 2007, **129**, 1506-1507.
6. E. Ohta, T. Nehira, H. Kawai, K. Fujiwara and T. Suzuki, *Tetrahedron Lett.*, 2008, **49**, 777-781.
7. J. Deng, N. Song, W. Liu, Q. Zhou and Z. Y. Wang, *Chemphyschem*, 2008, **9**, 1265-1269.
8. T. Suzuki, Y. Ishigaki, T. Iwai, H. Kawai, K. Fujiwara, H. Ikeda, Y. Kano and K. Mizuno, *Chem. Eur. J.*, 2009, **15**, 9434-9441.
9. J. K. Zak, M. Miyasaka, S. Rajca, M. Lapkowski and A. Rajca, *J. Am. Chem. Soc.*, 2010, **132**, 3246-3247.
10. S. Zahn and J. W. Canary, *Science*, 2000, **288**, 1404.
11. S. Zahn, D. Das and J. W. Canary, *Inorg. Chem.*, 2006, **45**, 6056-6063.
12. T. J. Katz, A. Sudhakar, M. F. Teasley, A. M. Gilbert, W. E. Geiger, M. P. Robben, M. Wuensch and M. D. Ward, *J. Am. Chem. Soc.*, 1993, **115**, 3182-3198.
13. E. Anger, M. Srebro, N. Vanthuyne, L. Toupet, S. Rigaut, C. Roussel, J. Autschbach, J. Crassous and R. Réau, *J. Am. Chem. Soc.*, 2012, **134**, 15628-15631.
14. T. Biet, A. Fihey, T. Cauchy, N. Vanthuyne, C. Roussel, J. Crassous and N. Avarvari, *Chem. Eur. J.*, 2013, **19**, 13160-13167.
15. D. Schweinfurth, M. Zalibera, M. Kathan, C. Shen, M. Mazzolini, N. Trapp, J. Crassous, G. Gescheidt and F. Diederich, *J. Am. Chem. Soc.*, 2014, **136**, 13045-13052.
16. M. Srebro, E. Anger, B. Moore Ii, N. Vanthuyne, C. Roussel, R. Réau, J. Autschbach and J. Crassous, *Chem. Eur. J.*, 2015, **21**, 17100-17115.
17. D. Li, Z. Y. Wang and D. Ma, *Chem. Commun.*, 2009, 1529-1531.
18. L. Pospíšil, L. Bednárová, P. Štěpánek, P. Slavíček, J. Vávra, M. Hromadová, H. Dlouhá, J. Tarábek and F. Teplý, *J. Am. Chem. Soc.*, 2014, **136**, 10826-10829.