Electronic Supplementary Information

Effect of cytosine–Ag^+–cytosine base pairing on the redox potential of the Ag^+/Ag couple and the chemical reduction of Ag^+ to Ag by tetrathiafulvalene

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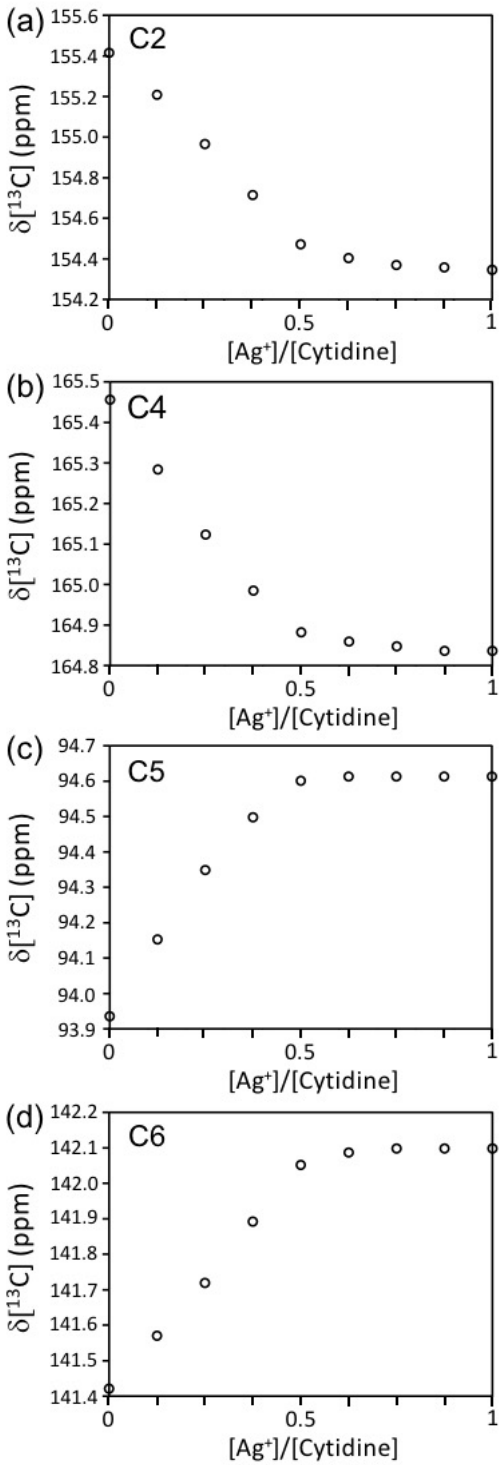

Fig. S1 ^{13}C NMR titration plots of cytidine with $AgNO_3$ in DMSO-d_6. Chemical shifts of the (a) C2, (b) C4, (c) C5, and (d) C6 carbons of cytidine are plotted against the molar ratio of [$AgNO_3$]/[Cytidine] (0–1 eq.). The concentration of cytidine is 0.5 M.

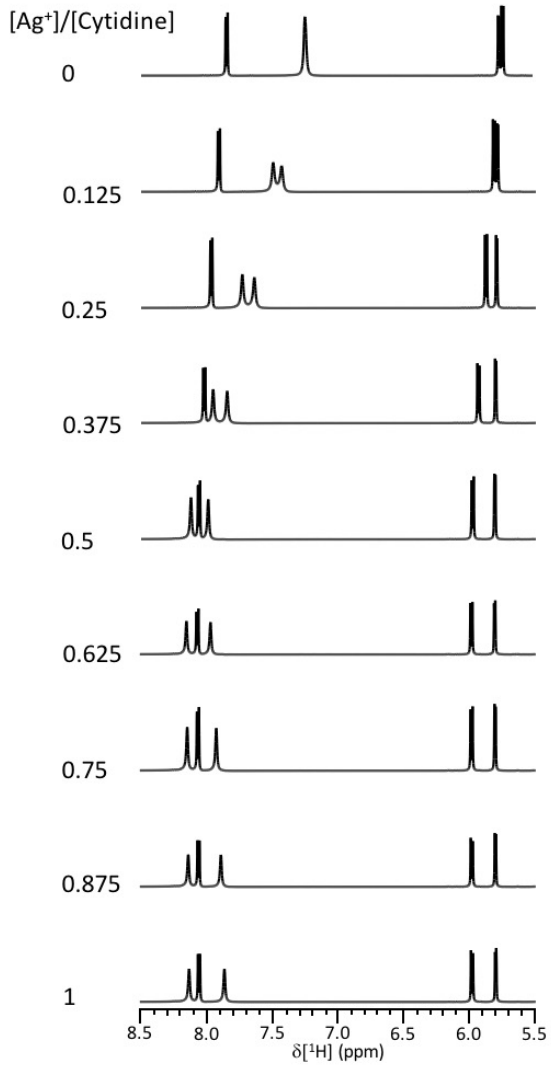

Fig. S2 H1′/H5/H6/-NH_2 peaks of cytidine observed in the 1D ^{1}H NMR spectra (500 MHz) during Ag^+-titration experiments in DMSO-d_6. The molar ratios of [$AgNO_3$]/[Cytidine] (0–1 eq.) are indicated on the left side of each spectrum. The concentration of cytidine is 0.5 M. The 1D ^{1}H NMR spectra were obtained using a JEOL ECZ 500 spectrometer at 298 K with 8 scans and 16384 points for a spectral width of 15024.04 Hz.

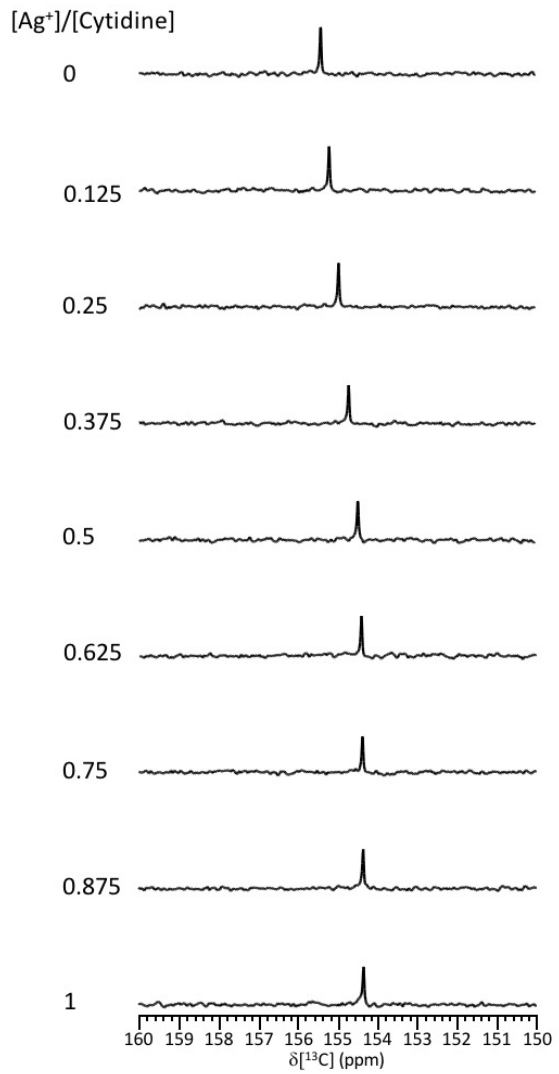

Fig. S3 C2 peak of cytidine observed in the 1D ^{13}C NMR spectra (126 MHz) during Ag^{+}-titration experiments in DMSO-d_6. The [$AgNO_3$]/[Cytidine] molar ratios (0–1 eq.) are indicated on the left side of each spectrum. The concentration of cytidine is 0.5 M. The 1D ^{13}C NMR spectra were obtained using a JEOL ECZ 500 spectrometer at 298 K with 32 scans and 32768 points for a spectral width of 47348.48 Hz.

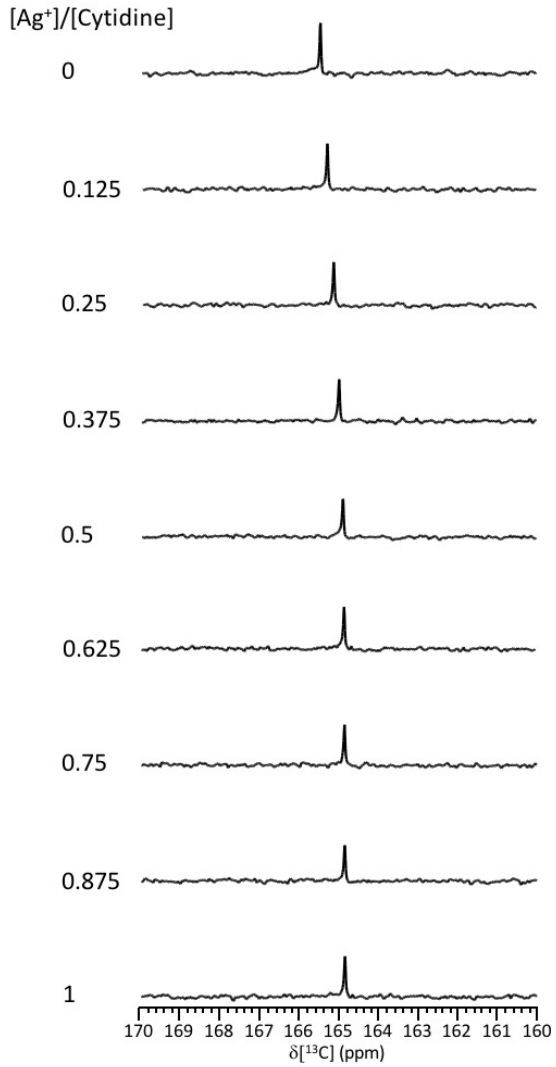

Fig. S4 C4 peak of cytidine observed in the 1D ^{13}C NMR spectra (126 MHz) during Ag^{+}-titration experiments in DMSO-d_6. The [$AgNO_3$]/[Cytidine] molar ratios (0–1 eq.) are indicated on the left side of each spectrum. The concentration of cytidine is 0.5 M. The 1D ^{13}C NMR spectra were obtained using a JEOL ECZ 500 spectrometer at 298 K with 32 scans and 32768 points for a spectral width of 47348.48 Hz.

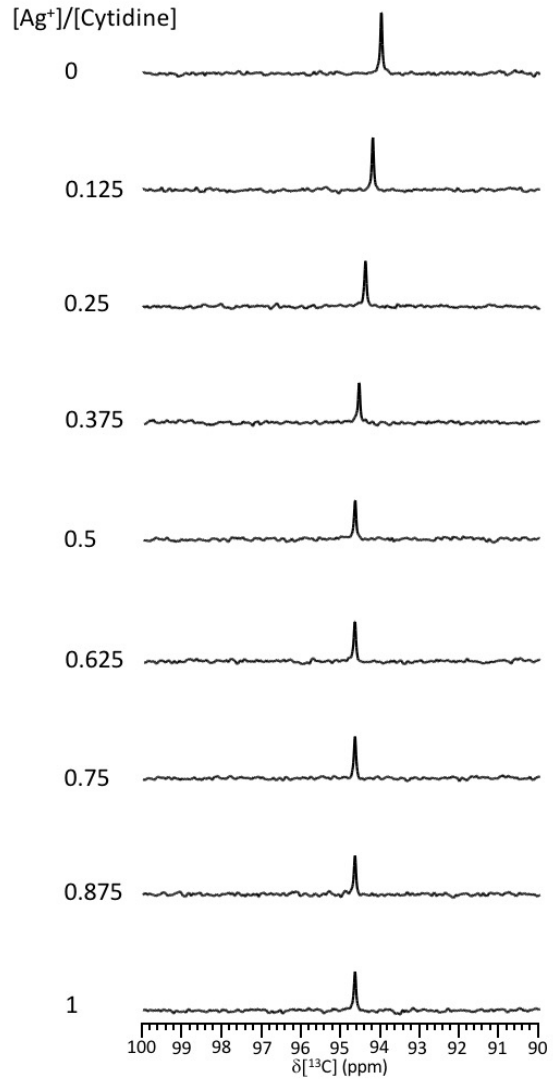

Fig. S5 C5 peak of cytidine observed in the 1D ^{13}C NMR spectra (126 MHz) during Ag^{+}-titration experiments in DMSO-d_6. The [$AgNO_3$]/[Cytidine] molar ratios (0–1 eq.) are indicated on the left side of each spectrum. The concentration of cytidine is 0.5 M. The 1D ^{13}C NMR spectra were obtained using a JEOL ECZ 500 spectrometer at 298 K with 32 scans and 32768 points for a spectral width of 47348.48 Hz.

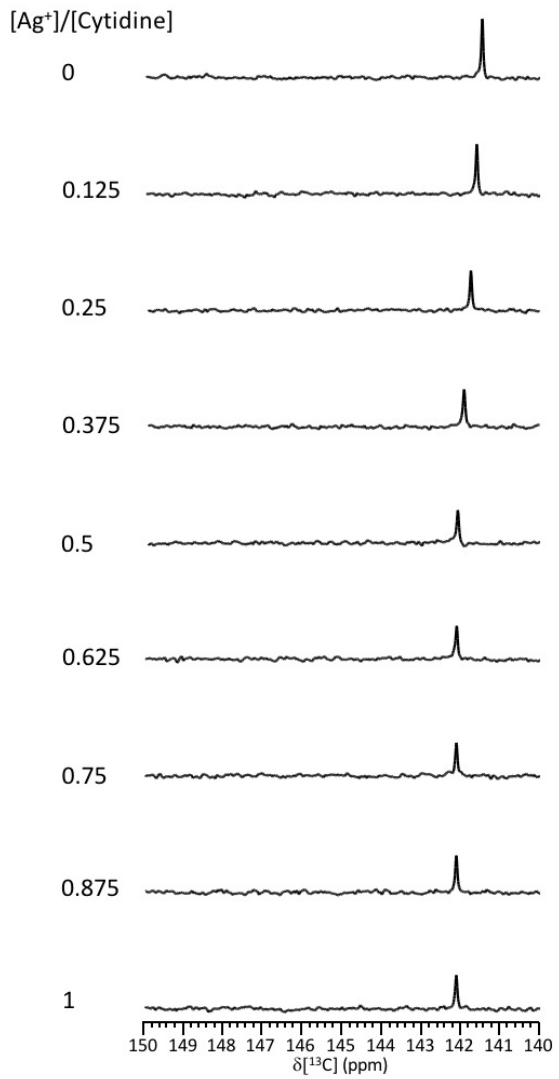

Fig. S6 C6 peak of cytidine observed in the 1D ^{13}C NMR spectra (126 MHz) during Ag^{+}-titration experiments in DMSO-d_6. The [$AgNO_3$]/[Cytidine] molar ratios (0–1 eq.) are indicated on the left side of each spectrum. The concentration of cytidine is 0.5 M. The 1D ^{13}C NMR spectra were obtained using a JEOL ECZ 500 spectrometer at 298 K with 32 scans and 32768 points for a spectral width of 47348.48 Hz.

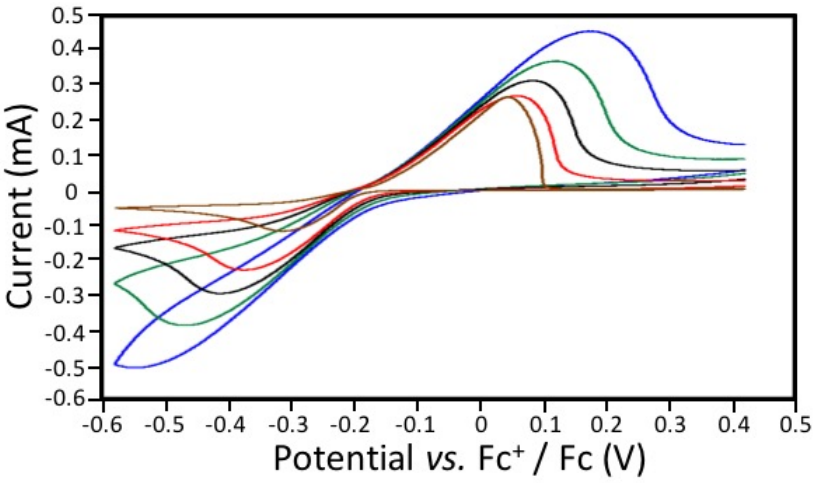

Fig. S7 Cyclic voltammograms of 30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate (V s^{-1}) = 0.01 (brown), 0.05 (red), 0.1 (black), 0.2 (green), 0.4 (blue).

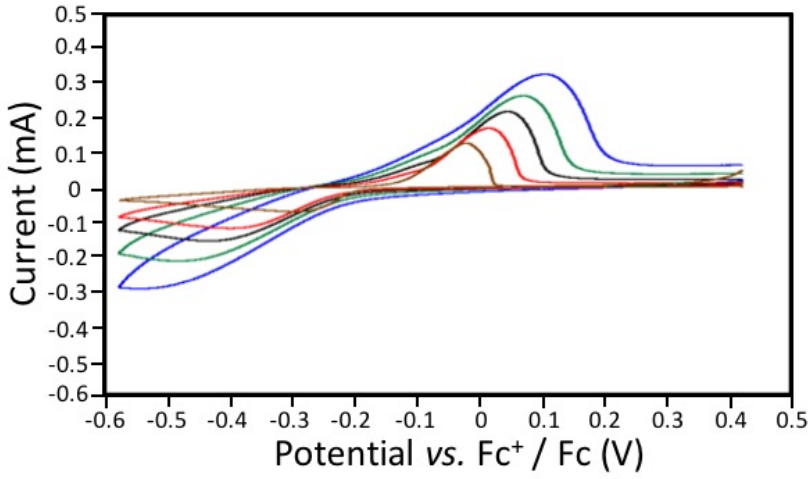

Fig. S8 Cyclic voltammograms of 30 mM cytidine/30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate (V s^{-1}) = 0.01 (brown), 0.05 (red), 0.1 (black), 0.2 (green), 0.4 (blue).

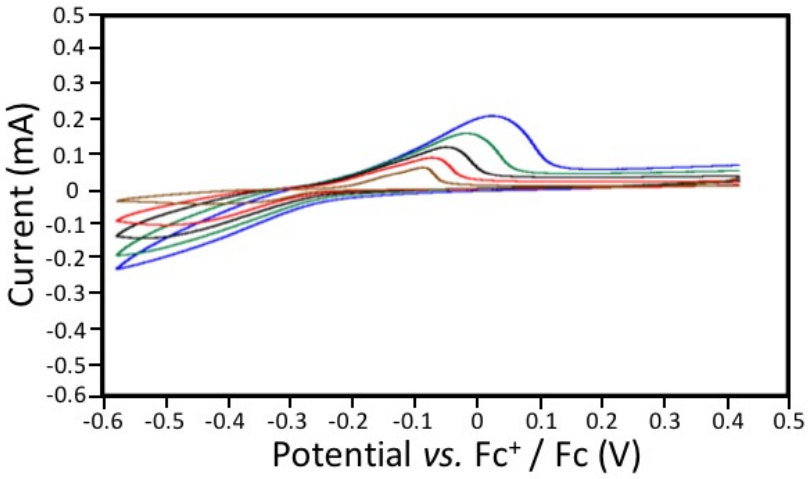

Fig. S9 Cyclic voltammograms of 60 mM cytidine/30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate (V s^{-1}) = 0.01 (brown), 0.05 (red), 0.1 (black), 0.2 (green), 0.4 (blue).

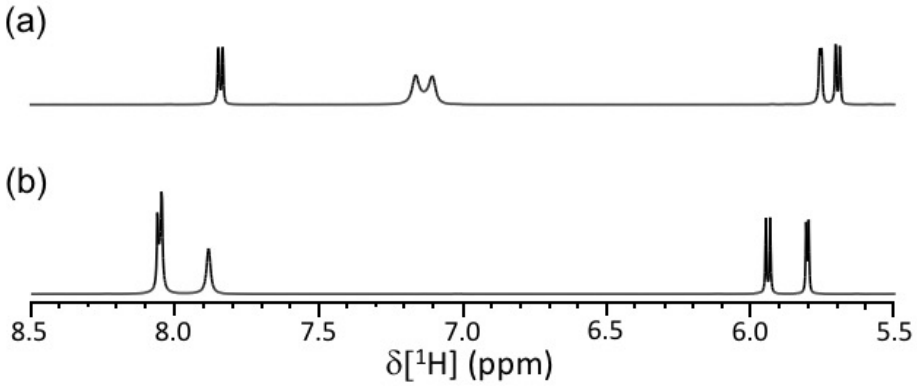

Fig. S10 H1′/H5/H6/-NH_2 peaks of cytidine observed in the 1D ^{1}H NMR spectra (500 MHz) of (a) 60 mM cytidine and (b) 60 mM cytidine/30 mM $AgNO_3$ in DMSO-d_6. The 1D ^{1}H NMR spectra were obtained using a JEOL ECA 500 spectrometer at 298 K with 32 scans and 16384 points for a spectral width of 15024.04 Hz.

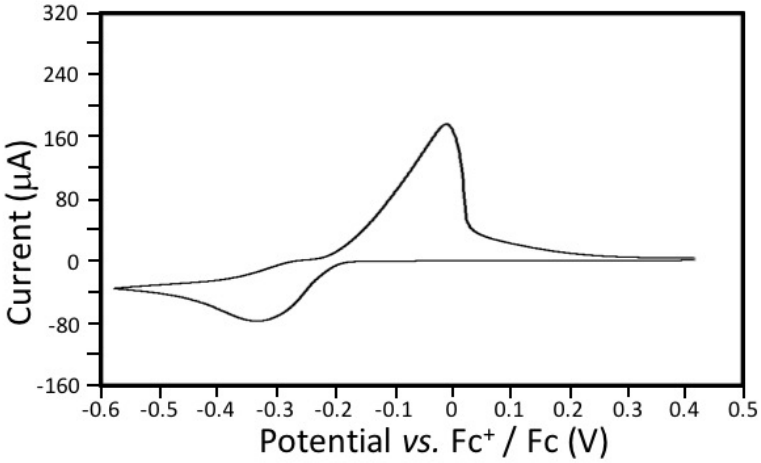

Fig. S11 Cyclic voltammogram of 60 mM guanosine/30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate = 0.01 V s^{-1}.

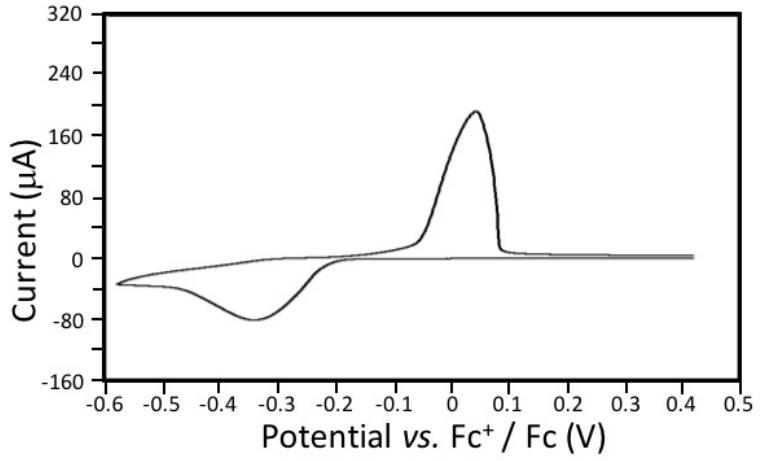

Fig. S12 Cyclic voltammogram of 60 mM adenosine/30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate = 0.01 V s^{-1}.

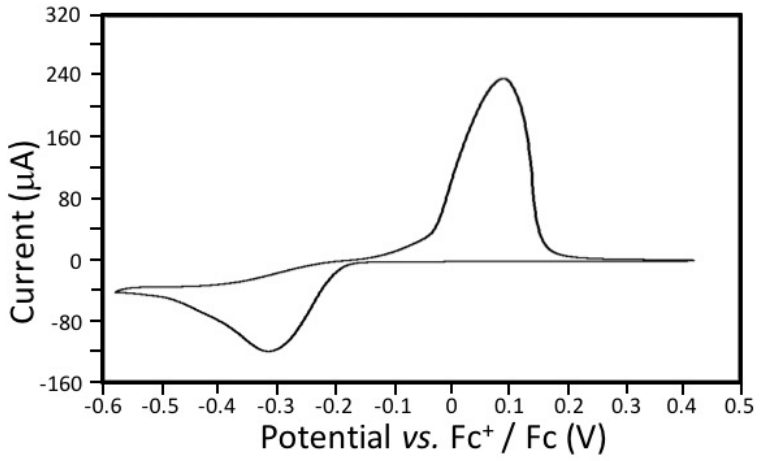

Fig. S13 Cyclic voltammogram of 60 mM thymidine/30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate = 0.01 V s^{-1}.

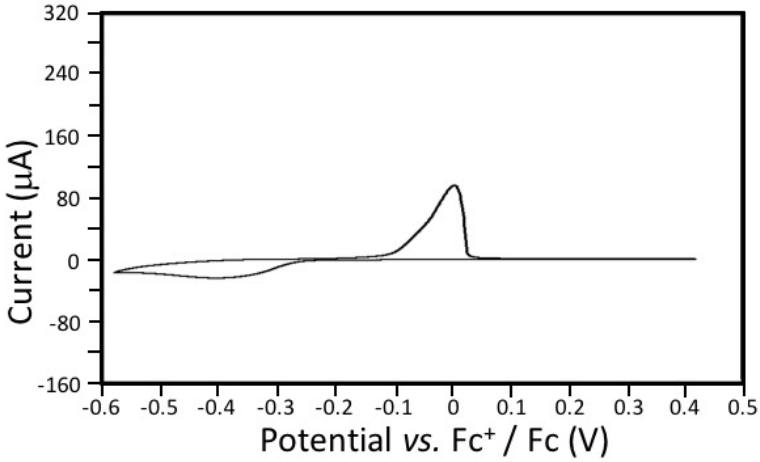

Fig. S14 Cyclic voltammogram of 60 mM 5-methylcytidine/30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate = 0.01 V s^{-1}.

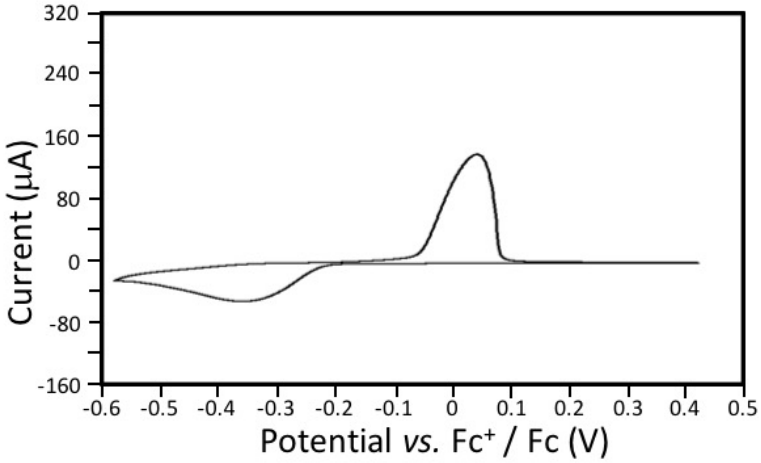

Fig. S15 Cyclic voltammogram of 60 mM 5-fluorocytidine/30 mM $AgNO_3$ in DMSO containing 100 mM $NaNO_3$ as a supporting electrolyte. Scan rate = 0.01 V s^{-1}.

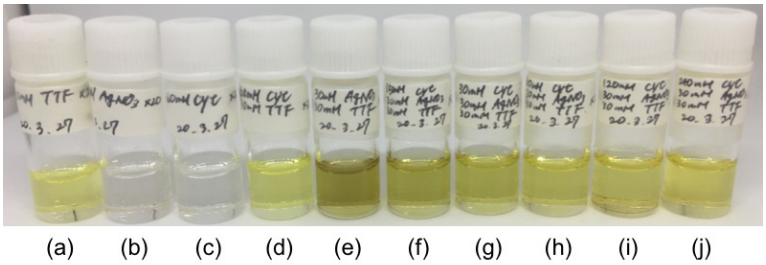

Fig. S16 Twenty-fold dilutions of solutions: (a) 1.5 mM TTF, (b) 1.5 mM $AgNO_3$, (c) 3 mM cytidine, and (d) 3 mM cytidine/1.5 mM TTF in DMSO and the supernatant fluids obtained from the centrifugation of cytidine:$AgNO_3$:TTF solutions with molar ratios of (e) 0:1:1, (f) 0.5:1:1, (g) 1:1:1, (h) 2:1:1, (i) 4:1:1, and (j) 8:1:1. Solutions before dilution can be seen in Fig. 6.

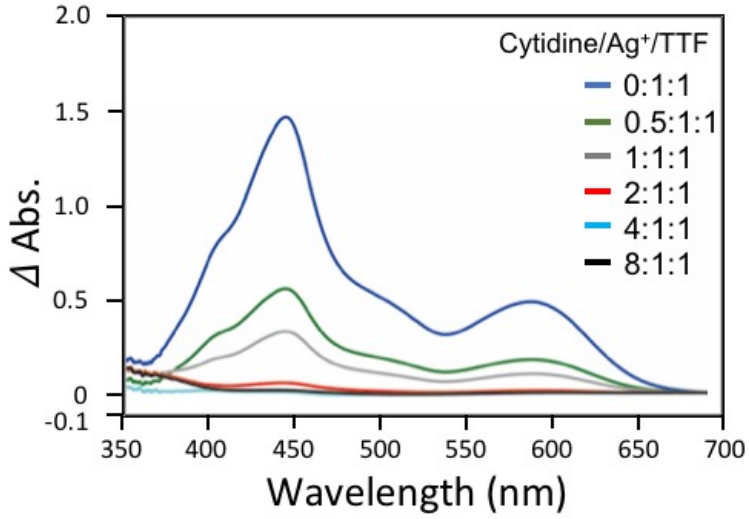

Fig. S17 UV–vis spectra obtained by subtracting the spectrum of 1.5 mM TTF (see Fig. S16, photograph (a)) from the spectra that were reported in Fig. 7. Molar ratio (cytidine:$AgNO_3$:TTF) = 0:1:1 (blue), 0.5:1:1 (green), 1:1:1 (gray), 2:1:1 (red), 4:1:1 (cyan), 8:1:1 (black).

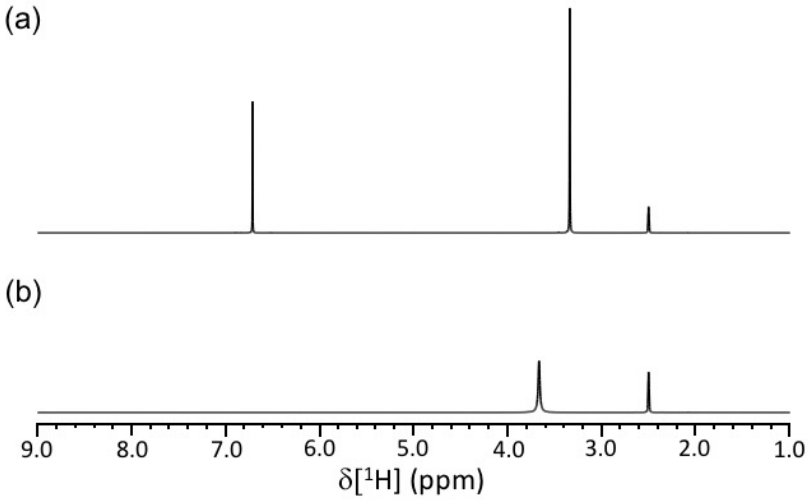

Fig. S18 1D ^{1}H NMR spectra (500 MHz) of (a) 30 mM TTF and (b) the supernatant fluid that was obtained from centrifuging 30 mM $AgNO_3$/30 mM TTF in DMSO-d_6. The ^{1}H NMR signal of TTF (δ ^{1}H = 6.71) disappeared after 1 equivalent of $AgNO_3$ was added. The 1D ^{1}H NMR spectra were obtained using a JEOL ECZ 500 spectrometer at 298 K with 64 scans and 16384 points for a spectral width of 15024.04 Hz.