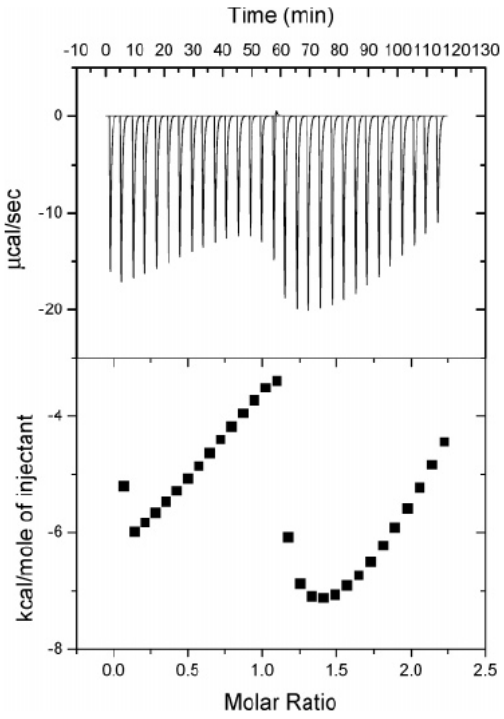


Figure S1. Two step binding of heat effects of complexation of BnV^{2+} (10.5 mmol) with STC4A (1.06 mmol) for each injection during the titration microcalorimetric experiment (*Cryst. Growth Des.* **2005**, *5*, 231−235).

Table S1. Chemical Shift Changes ($\Delta\delta$, ppm) of MV^{2+} Protons in the Presence of STC4A at pD 7.2[a,b]

host	CH_3	*a*-H	*b*-H
STC4A	–0.71	–0.88	–0.86

[a] $\Delta\delta = \delta$(presence of 1 equiv of host) – δ(free guest). Negative values indicate upfield shift. [b] The host and guest were mixed in a 1:1 stoichiometry at 10 mM.

Table S2. Chemical Shift Changes ($\Delta\delta$, ppm) of EV^{2+} Protons in the Presence of SC4A, SC5A and STC4A at pD 7.2[a,b]

host	CH_3	CH_2	*a*-H	*b*-H
SC4A	–1.12	–1.10	–0.64	–0.25
SC5A	–0.47	–0.74	–0.93	–0.95
STC4A	–0.48	–0.68	–0.69	–0.60

[a] $\Delta\delta = \delta$(presence of 1 equiv of host) – δ(free guest). Negative values indicate upfield shift. [b] The host and guest were mixed in a 1:1 stoichiometry at 10 mM.

Table S3. Chemical Shift Changes ($\Delta\delta$, ppm) of PV^{2+} Protons in the Presence of SC4A, SC5A and STC4A at pD 7.2[a,b]

host	CH_3	CH_2-1	CH_2-2	*a*-H	*b*-H
SC4A	–1.10	–1.30	–1.23	–0.57	–0.15
SC5A	–0.46	–0.63	–0.82	–1.04	–0.95
STC4A	–0.71	–0.71	–0.69	–0.51	–0.32

[a] $\Delta\delta = \delta$(presence of 1 equiv of host) – δ(free guest). Negative values indicate upfield shift. [b] The host and guest were mixed in a 1:1 stoichiometry at 10 mM.

Table S4. Chemical Shift Changes ($\Delta\delta$, ppm) of BV^{2+} Protons in the Presence of SC4A, SC5A and STC4A at pD 7.2[a,b]

host	CH_3	CH_2-1	CH_2-2	CH_2-3	*a*-H	*b*-H
SC4A	–0.93	–0.87	–0.89	–0.81	–0.38	–0.12
SC5A	–0.30	–0.51	–0.58	–0.73	–0.88	–0.81
STC4A	–0.58	–0.59	–0.51	–0.49	–0.31	–0.17

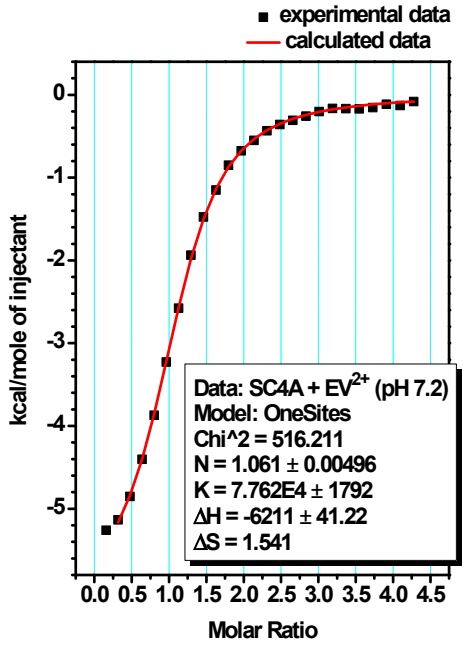
[a] $\Delta\delta = \delta$(presence of 1 equiv of host) – δ(free guest). Negative values indicate upfield shift. [b] The host and guest were mixed in a 1:1 stoichiometry at 10 mM.

Table S5. Chemical Shift Changes ($\Delta\delta$, ppm) of BnV^{2+} Protons in the Presence of SC4A and SC5A at pD 7.2[a,b]

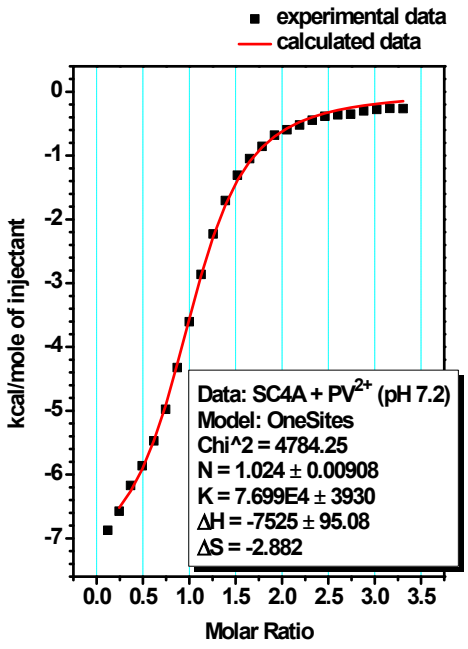
host	H-1	H-2	H-3	CH_2	*a*-H	*b*-H
SC4A	–1.36	–1.14	–0.83	–0.57	–0.43	–0.19
SC5A	–0.36	–0.44	–0.72	–0.97	–1.03	–0.89

[a] $\Delta\delta = \delta$(presence of 1 equiv of host) – δ(free guest). Negative values indicate upfield shift. [b] The host and guest were mixed in a 1:1 stoichiometry at 10 mM.

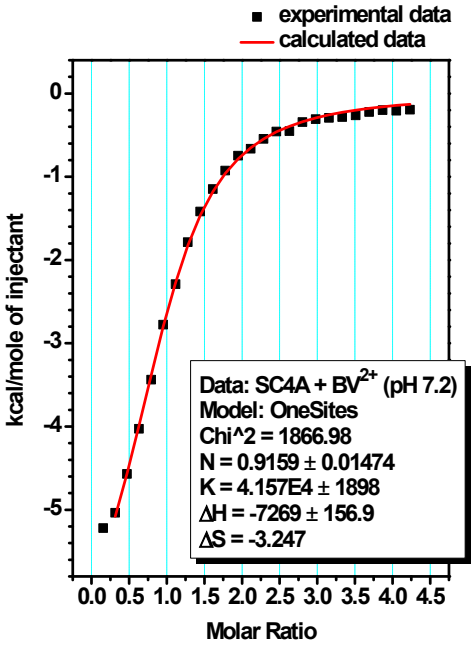
ITC Curves:



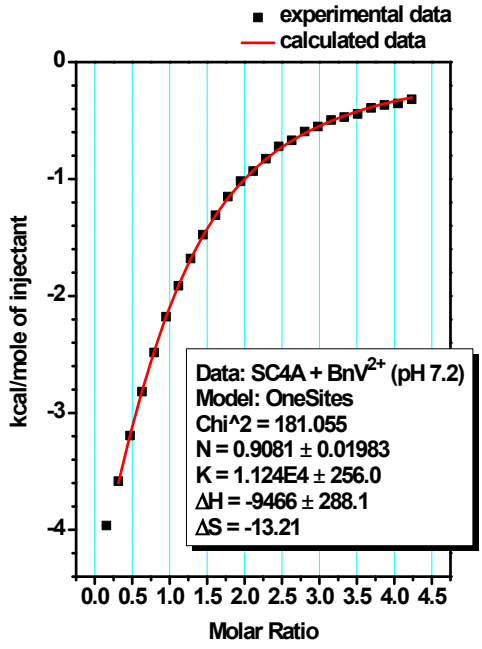
(a)



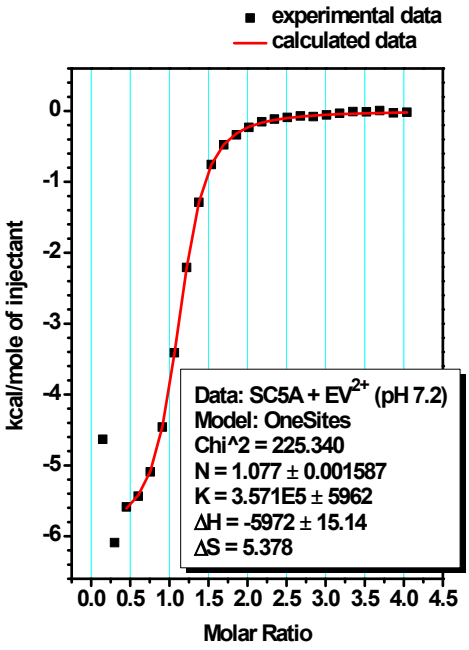
(b)



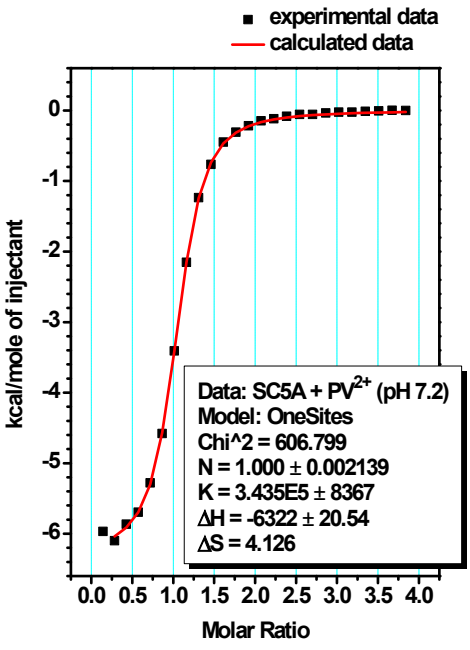
(c)



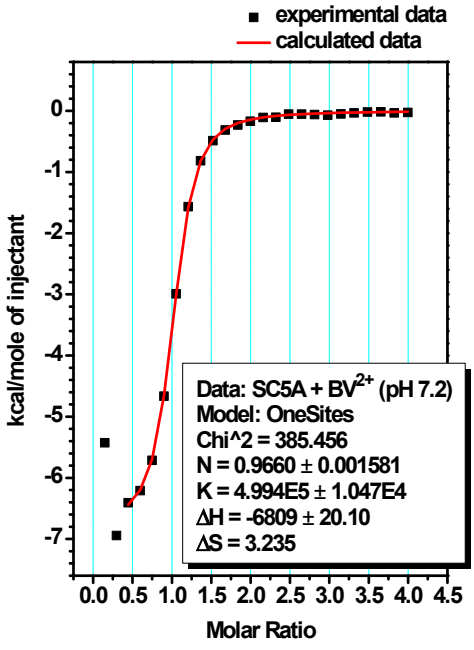
(d)


experimental data
calculated data
kcal/mole of injectant
Molar Ratio
Data: SC5A + EV2+ (pH 7.2)
Model: OneSites
Chi^2 = 225.340
N = 1.077 ± 0.001587
K = 3.571E5 ± 5962
ΔH = -5972 ± 15.14
ΔS = 5.378

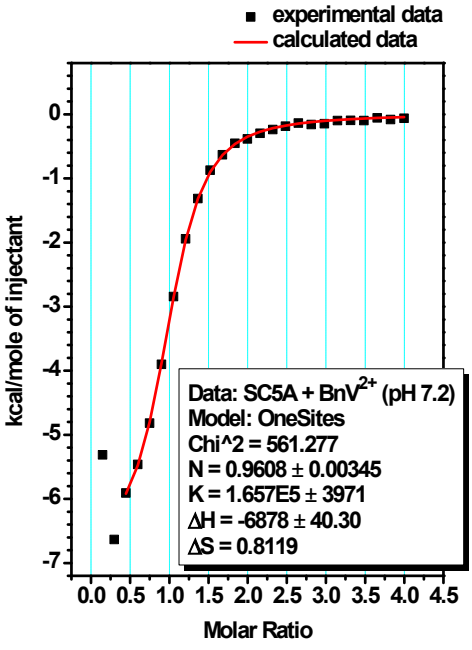
(e)


experimental data
calculated data
kcal/mole of injectant
Molar Ratio
Data: SC5A + PV2+ (pH 7.2)
Model: OneSites
Chi^2 = 606.799
N = 1.000 ± 0.002139
K = 3.435E5 ± 8367
ΔH = -6322 ± 20.54
ΔS = 4.126

(f)


experimental data
calculated data
kcal/mole of injectant
Molar Ratio
Data: SC5A + BV2+ (pH 7.2)
Model: OneSites
Chi^2 = 385.456
N = 0.9660 ± 0.001581
K = 4.994E5 ± 1.047E4
ΔH = -6809 ± 20.10
ΔS = 3.235

(g)


experimental data
calculated data
kcal/mole of injectant
Molar Ratio
Data: SC5A + BnV2+ (pH 7.2)
Model: OneSites
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N = 0.9608 ± 0.00345
K = 1.657E5 ± 3971
ΔH = -6878 ± 40.30
ΔS = 0.8119

(h)

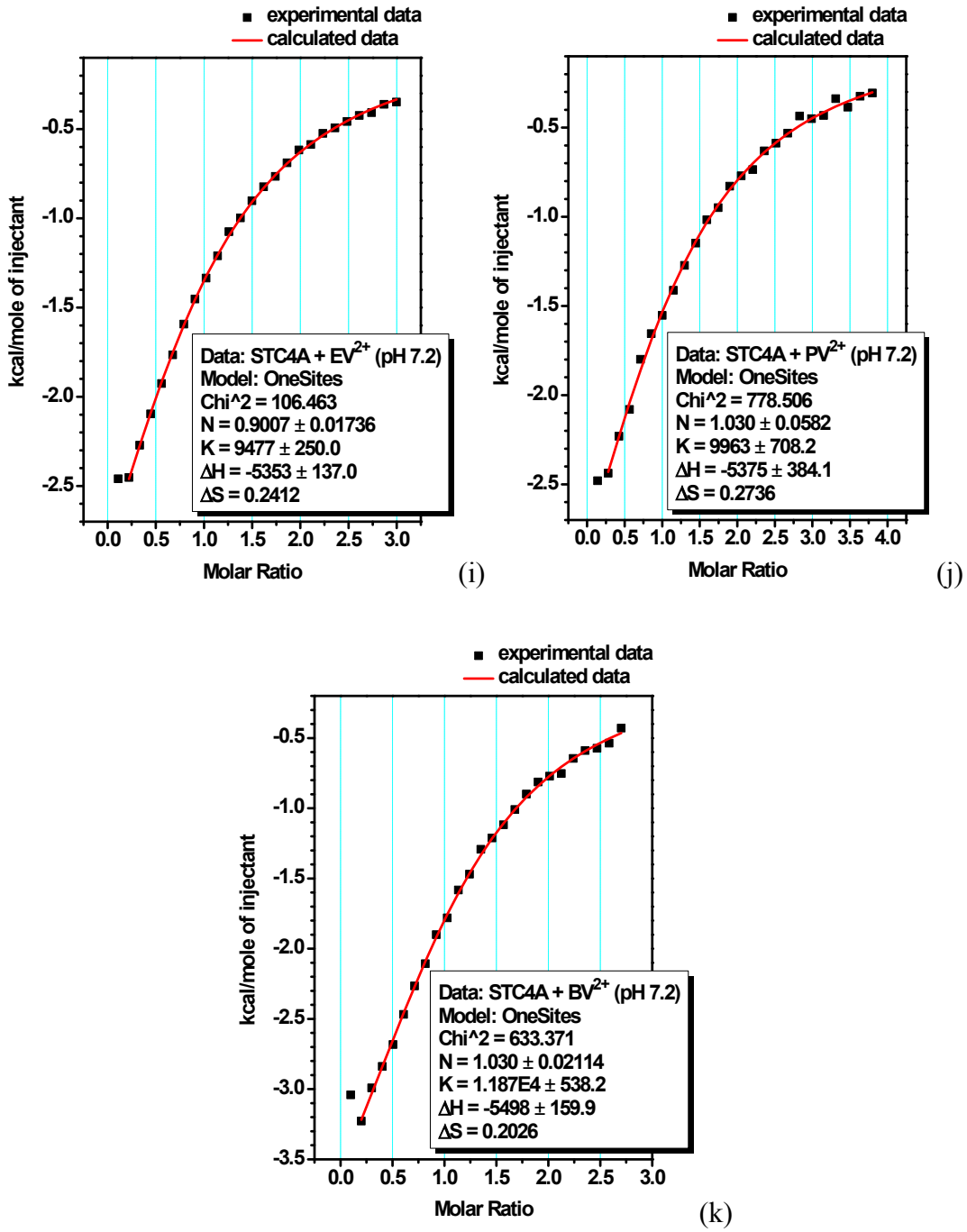

Figure S2. "Net" heat effects of complexation of viologens with SC4A, SC5A, and STC4A for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using the "one set of binding sites" model.