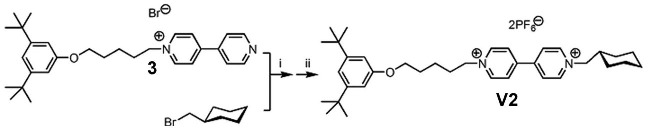
Supporting Information

Deutman et al. 10.1073/pnas.0810145106



Scheme S1. Synthesis of viologen derivative **V2**. (*i*) DMF 95 °C, 3 days; (*ii*) NH$_4$PF$_6$(aq).

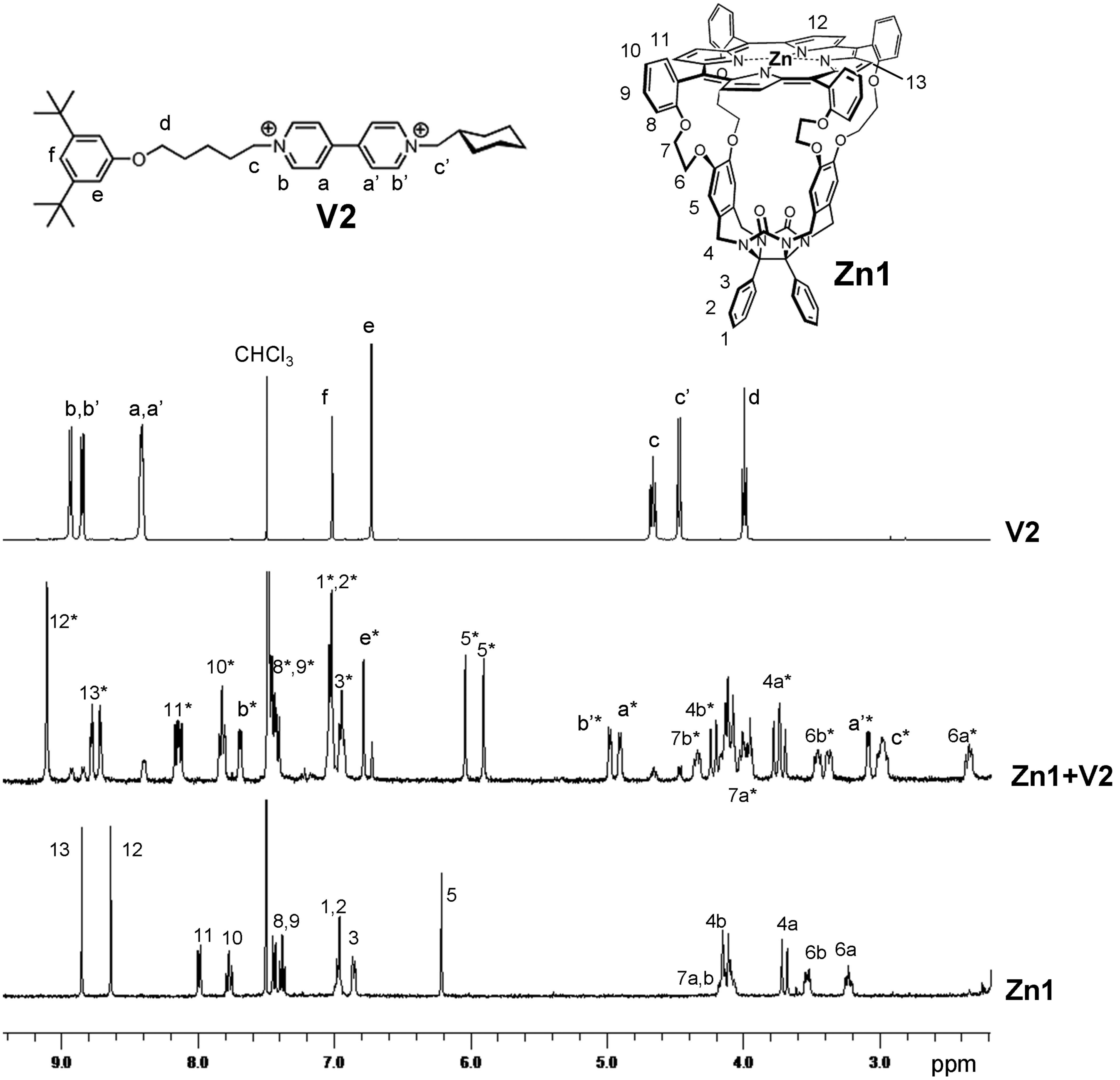


Fig. S1. ^{1}H NMR spectra (400 MHz in 1:1 (vol/vol) $CD_3CN/CDCl_3$ at 298 K) with assignments of **Zn1**, **V2** and a mixture of **Zn1** and 1.2 equivalents of **V2**.

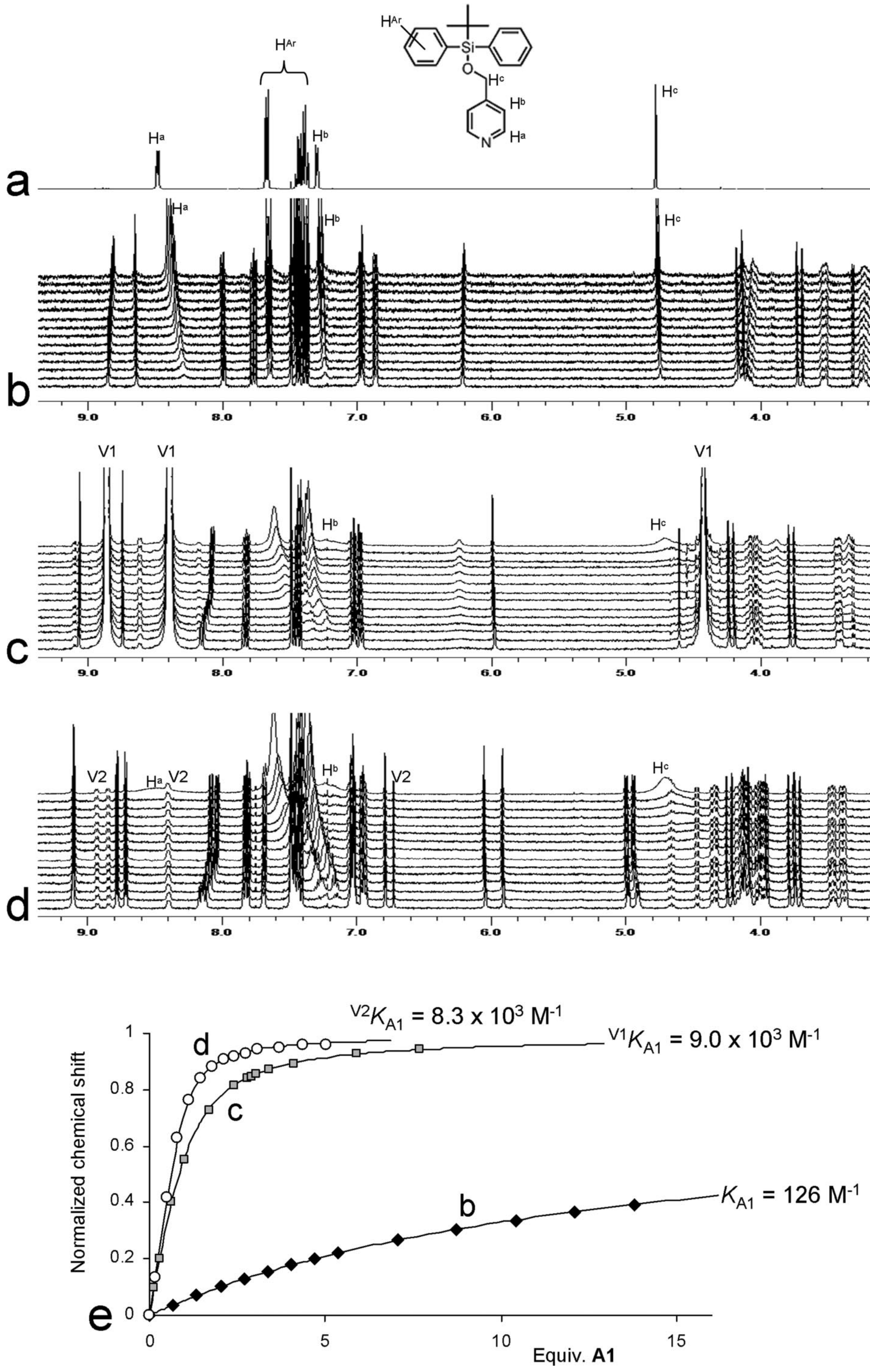


Fig. S2. ^{1}H NMR (400 MHz in 1:1 (vol/vol) $CD_3CN/CDCl_3$ at 298 K) binding experiments. (*a*) Spectrum of **A1**. (*b*) ^{1}H NMR titration experiment of **Zn1** with (from bottom to top increasing concentrations of) **A1**. (*c*) ^{1}H NMR titration experiment of a mixture of **Zn1** and an excess of **V1** with (from bottom to top increasing concentrations of) **A1**. (*d*) ^{1}H NMR titration experiment of the pseudorotaxane complex between **Zn1** and **V2** with (from bottom to top increasing concentrations of) **A1**. (*e*) The obtained normalized binding isotherms from the titration experminents (*b*, *c*, and *d* as above) with the fits according to a 1:1 receptor–guest binding process.

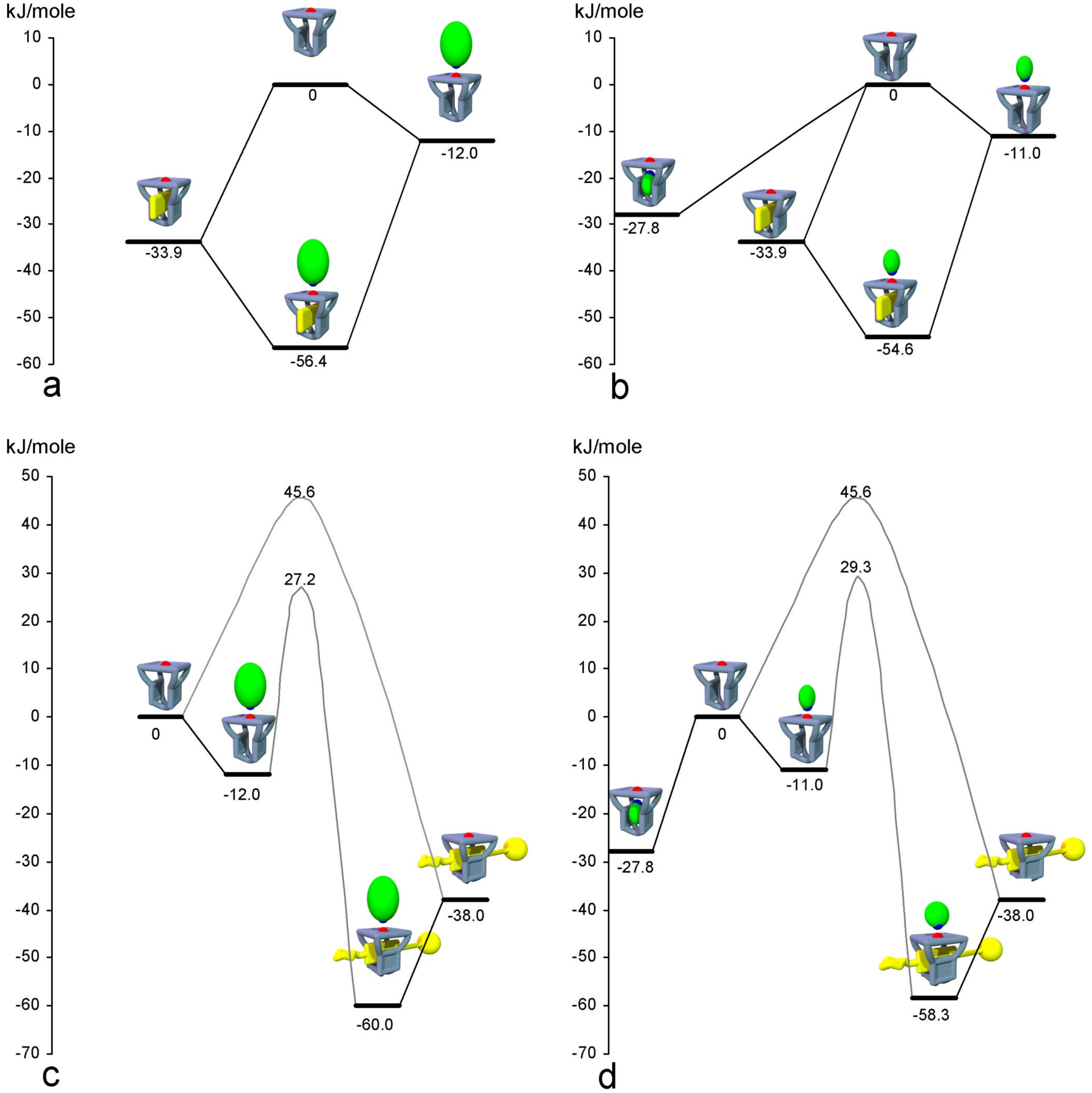


Fig. S3. Energy diagrams of the coooperative binding circles with the binding free energies of the 1:1 and ternary complexes, and the activation energies of the slippage process as experimentally derived. (*a*) The combination **Zn1**, **A1**, and **V1**. (*b*) The combination **Zn1**, **A2**, and **V1**. (*c*) The combination **Zn1**, **A1**, and **V2**. (*d*) The combination **Zn1**, **A2**, and **V2**.

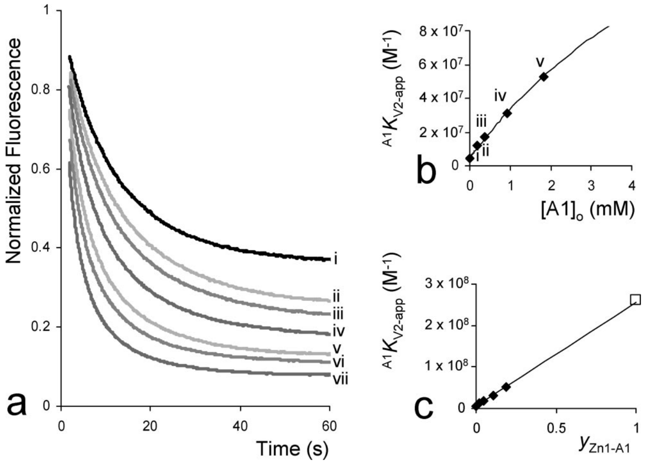


Fig. S4. Fluorescence slippage experiments between **V2** and **Zn1** in the presence of **A1**. (*a*) Fluorescence emission as a function of time upon the addition of 1 equivalent of **V2** to **Zn1** (0.8 μM) in the presence of increasing concentrations (from *i* to *vii*) of **A1**. (*b*) Calculated rate constants $^{A1}K_{V2\text{-}app}$ plotted vs. the concentration of **A1** and the fit according to Eq. **1**. (*c*) Linear relationship between the value of $^{A1}K_{V2\text{-}app}$ and the fractional saturation of **Zn1** with **A1** ($y_{Zn1\text{-}A1}$) according to Eq. **3**.

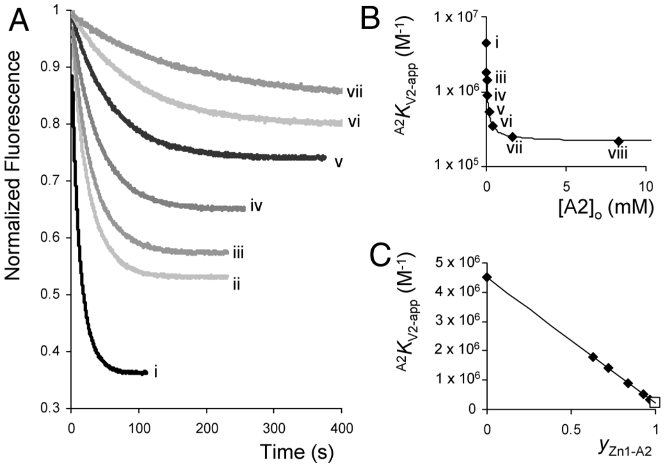


Fig. S5. Fluorescence slippage experiments between **V2** and **Zn1** in the presence of increasing concentrations of **A2**. (*A*) Fluorescence emission as a function of time upon the addition of 1 equivalent of **V2** to **Zn1** (μM) in the presence of increasing concentrations (from *i* to *vii*) of **A2**. (*B*) Calculated rate constants $^{A2}K_{V2\text{-app}}$ plotted vs. the concentration of **A2** and the fit according to Eq. **4**. (*C*) Linear relationship of the value of $^{A2}K_{V2\text{-app}}$ and the fractional saturation of **Zn1** with **A2** ($y_{Zn1\text{-}A2}$) according to Eq. **5**.

Table S1. Measured association constants [$^{G2}K_{G1}$ (M^{-1})] of titration experiments of guests (G1) to Zn1 in the presence and absence of the other guest (G2) and the measured rate constants of complex formation [$^{G2}k_{on}$ ($M^{-1}s^{-1}$)] and complex dissociation [$^{G2}k_{off}$ (s^{-1})] between V2 and Zn1 via slippage in the presence of different concentrations of pyridine ligands A1 and A2

G1	G2 ([G2]$_o$)	$^{G2}K_{G1}$[††]	$^{G2}k_{on}$[**]	$^{G2}k_{off}$[††]
A1	–	$1.3\times 10^{2*\dagger}$		
A2	–	$7.5\times 10^{4\dagger}$		
A1	**V1 (full)**	$9.0\times 10^{3*\dagger}$		
A1	**V2 (full)**	$8.3\times 10^{3*}$		
V1	–	$8.6\times 10^{5\ddagger}$		
V1	**A1** (2.1×10^{-4})	$2.2\times 10^{6\ddagger}$		
V1	**A1** (7.4×10^{-4})	$5.3\times 10^{6\ddagger}$		
V1	**A1** (1.5×10^{-3})	$9.7\times 10^{6\ddagger}$		
V1	**A1** (2.9×10^{-3})	$1.5\times 10^{7\ddagger}$		
V1	**A1** (6.7×10^{-3})	$2.7\times 10^{7\ddagger}$		
V1	**A1 (full)**	**$6.5\times 10^{7\S}$**		
V1	**A2** (9.0×10^{-6})	$5.6\times 10^{5\ddagger}$		
V1	**A2** (1.8×10^{-5})	$4.2\times 10^{5\ddagger}$		
V1	**A2** (4.4×10^{-5})	$2.5\times 10^{5\ddagger}$		
V1	**A2** (8.8×10^{-5})	$1.6\times 10^{5\ddagger}$		
V1	**A2** (1.7×10^{-4})	$1.1\times 10^{5\ddagger}$		
V1	**A2** (4.0×10^{-4})	$8.5\times 10^{4\ddagger}$		
V1	**A2** (7.2×10^{-4})	$7.3\times 10^{4\ddagger}$		
V1	**A2 (full)**	**$5.8\times 10^{4\S}$**		
V2	–	$4.5\times 10^{6\ddagger}$	$6.4\times 10^{4\ddagger}$	
V2	**A1** (1.9×10^{-4})	$1.2\times 10^{7\ddagger}$	$8.6\times 10^{4\ddagger}$	
V2	**A1** (3.7×10^{-4})	$1.7\times 10^{7\ddagger}$	$1.0\times 10^{5\ddagger}$	
V2	**A1** (9.2×10^{-4})	$3.1\times 10^{7\ddagger}$	$1.5\times 10^{5\ddagger}$	
V2	**A1** (1.8×10^{-3})	$5.3\times 10^{7\ddagger}$	$2.1\times 10^{5\ddagger}$	
V2	**A1** (3.3×10^{-3})	[‡‡]	$2.9\times 10^{5\ddagger}$	
V2	**A1** (6.4×10^{-3})	[‡‡]	$4.2\times 10^{5\ddagger}$	
V2	**A1 (full)**	**$2.6\times 10^{8\S}$**	**$8.4\times 10^{5\S}$**	
V2	–	$4.5\times 10^{6\ddagger}$		$1.4\times 10^{-2\ddagger}$
V2	**A1** (1.9×10^{-4})	$1.2\times 10^{7\ddagger}$		$7.3\times 10^{-3\ddagger}$
V2	**A1** (3.7×10^{-4})	$1.8\times 10^{7\ddagger}$		$6.0\times 10^{-3\ddagger}$
V2	**A1** (9.2×10^{-4})	$3.2\times 10^{7\ddagger}$		$4.3\times 10^{-3\ddagger}$
V2	**A1 (full)**	**$2.8\times 10^{8\S}$**		**$3.1\times 10^{-3\S}$**
V2	**A2** (2.3×10^{-5})	$1.8\times 10^{6\ddagger}$	$2.4\times 10^{4\ddagger}$	
V2	**A2** (3.5×10^{-5})	$1.4\times 10^{6\ddagger}$	$1.8\times 10^{4\ddagger}$	
V2	**A2** (6.9×10^{-5})	$9.0\times 10^{5\ddagger}$	$1.1\times 10^{4\ddagger}$	
V2	**A2** (1.7×10^{-4})	$5.3\times 10^{5\ddagger}$	$5.0\times 10^{3\ddagger}$	
V2	**A2** (4.3×10^{-4})	$3.5\times 10^{5\ddagger}$	$2.5\times 10^{3\ddagger}$	
V2	**A2** (1.7×10^{-3})	$2.5\times 10^{5\ddagger}$	$1.1\times 10^{3\ddagger}$	
V2	**A2** (8.3×10^{-3})	$2.2\times 10^{5\ddagger}$	$6.8\times 10^{2\ddagger}$	
V2	**A2 (full)**	**$2.2\times 10^{5\S}$**	**$6.8\times 10^{2\S}$**	
V2	**A2** (5.6×10^{-5})	$1.2\times 10^{6\ddagger}$		$1.0\times 10^{-2\ddagger}$
V2	**A2** (1.4×10^{-4})	$7.5\times 10^{5\ddagger}$		$8.4\times 10^{-3\ddagger}$
V2	**A2** (3.5×10^{-4})	$6.1\times 10^{5\ddagger}$		$6.0\times 10^{-3\ddagger}$
V2	**A2** (1.4×10^{-3})	$3.8\times 10^{5\ddagger}$		$4.1\times 10^{-3\ddagger}$
V2	**A2 (full)**	**$3.6\times 10^{5\S}$**		**$3.2\times 10^{-3\ddagger}$**

The calculated values of the magnitudes of the constants upon full saturation of Zn1 with the second guest present in solution are presented in bold type.

[*] Determined by ^{1}H NMR titrations ([**Zn1**]$_o$ ≈ mM) in 1:1 (vol/vol) $CDCl_3/CD_3CN$ at 298 K.

[†] Determined by UV-vis titrations ([**Zn1**]$_o$ ≈ μM) in 1:1 (vol/vol) acetonitrile/chloroform at 298 K.

[‡] Determined by fluorescence titrations and kinetic experiments ([**Zn1**]$_o$ ≈ μM) in 1:1 (vol/vol) acetonitrile/chloroform at 298 K.

[§] The calculated value based on the titration series in which $y_{Zn1\text{-}G2} = 1$.

[**] Estimated error <15%.

[††] Estimated error <35%.

[‡‡] Values too high to determine accurately at the used experimental concentrations.

Other Supporting Information Files

SI Appendix (PDF)