Supplementary Figures and Tables

Interactions of Boron Clusters and their Derivatives with Serum Albumin

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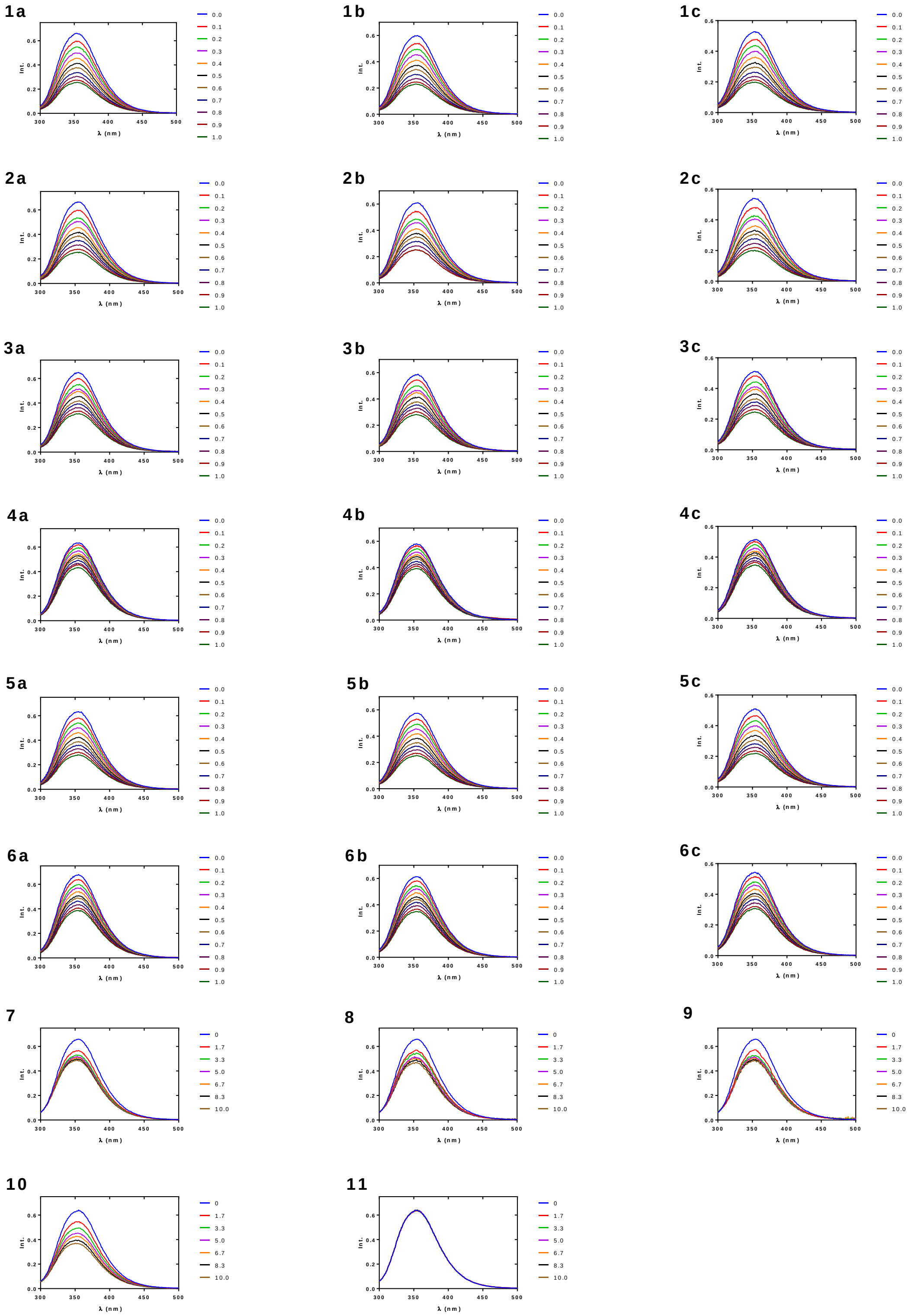

Figure S1. Fluorescence emission spectra of BSA (10.5 µM) in the presence of boron cluster and their derivatives in 0.10 M sodium bicarbonate (pH 8.4) with 2% DMSO, λ_{ex}=280 nm. Numbers **1** to **11** are symbols of the boron compounds, whereas letters **a**, **b** and **c** show the temperature at which the measurement was performed (25, 31 and 37°C, respectively). Measurements for compounds **7** to **11** were performed only at 25°C. The concentration of **1** to **6** was 0 to 10.5 µM with 1.05 µM intervals; the concentration of **7** to **11** was 0 to 105 µM with 17.5 µM intervals. Detailed molar excess of boron cluster is described in the legend.

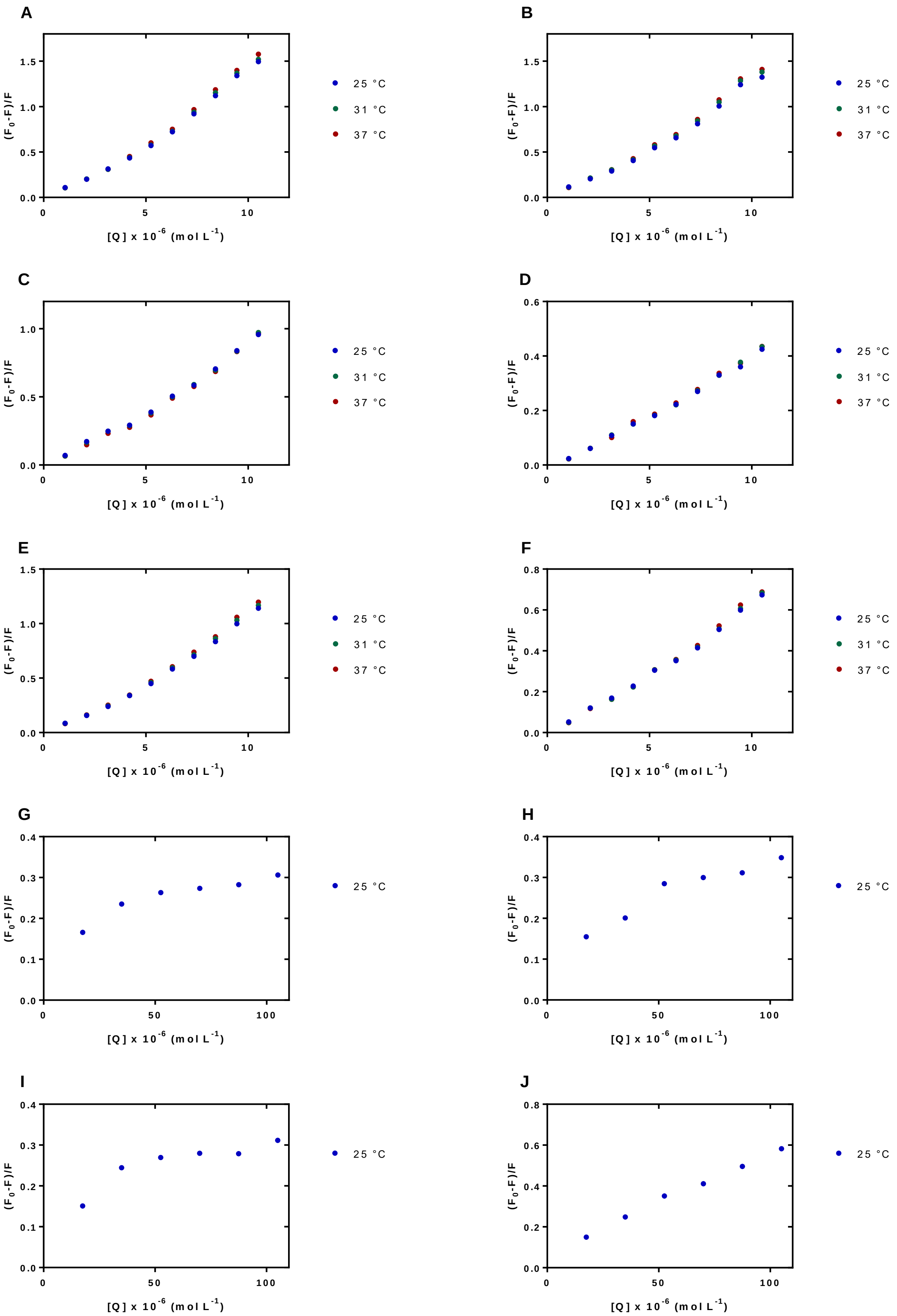

Figure S2. Stern-Volmer plots for the binding of BSA with compounds **1** (A), **2** (B), **3** (C), **4** (D), **5** (E), **6** (F), **7** (G), **8** (H), **9** (I) and **10** (J) at various temperatures (25, 31 and 37°C).

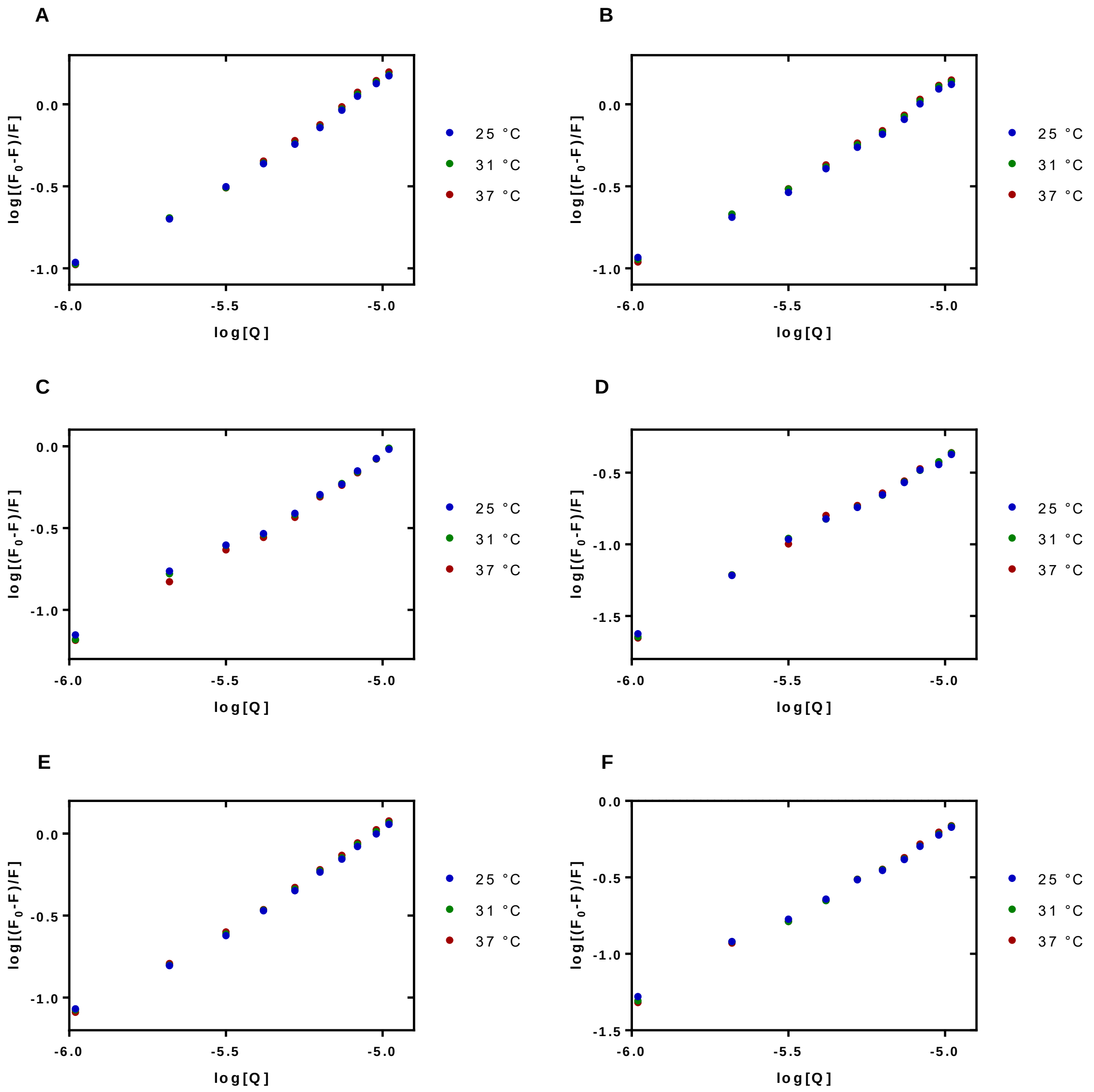

Figure S3. Double-logarithmic plots for the binding of BSA with compounds **1** (A), **2** (B), **3** (C), **4** (D), **5** (E) and **6** (F) at various temperatures (25, 31 and 37°C).

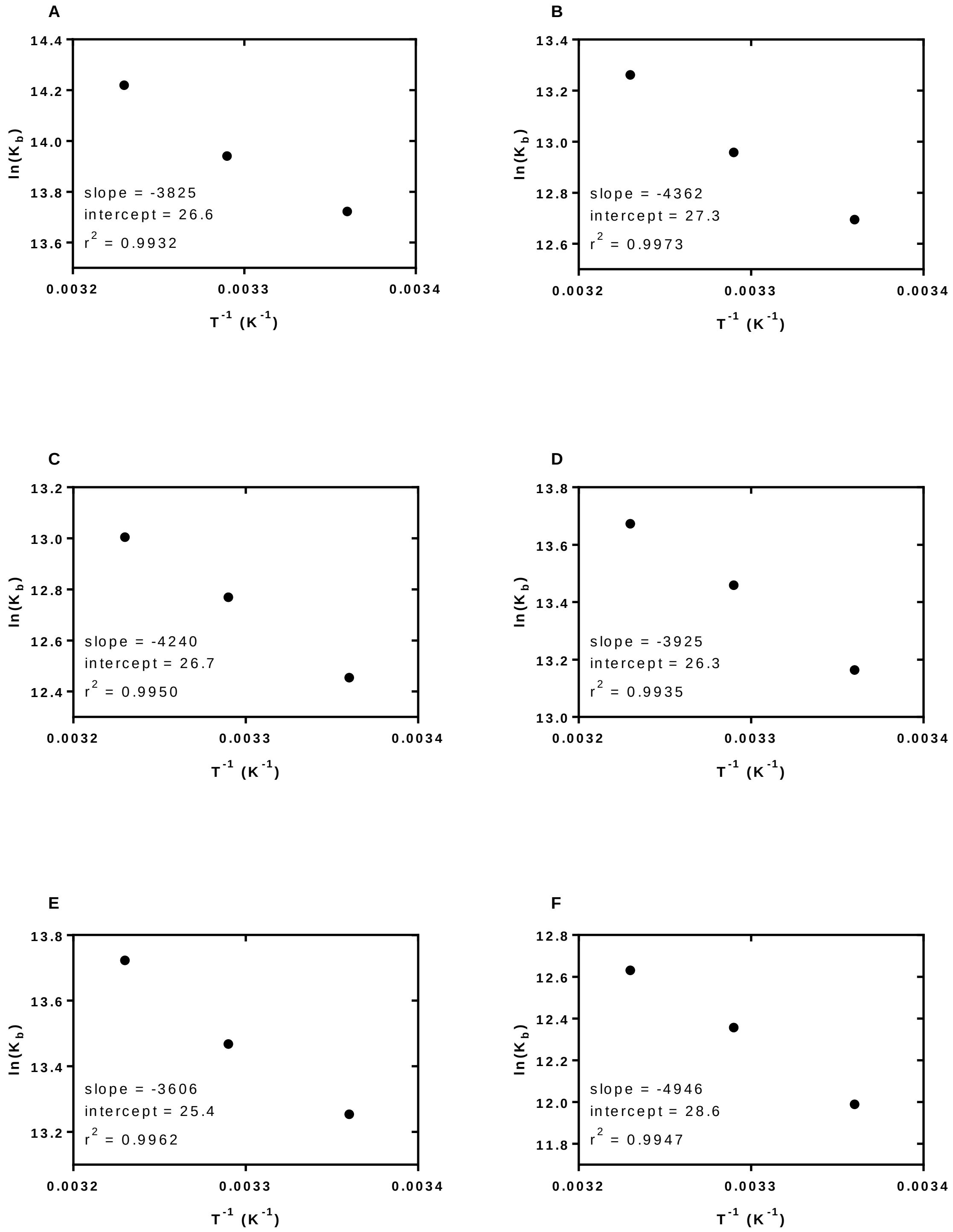

Figure S4. Van't Hoff plots for the binding of BSA with compounds **1** (A), **2** (B), **3** (C), **4** (D), **5** (E) and **6** (F).

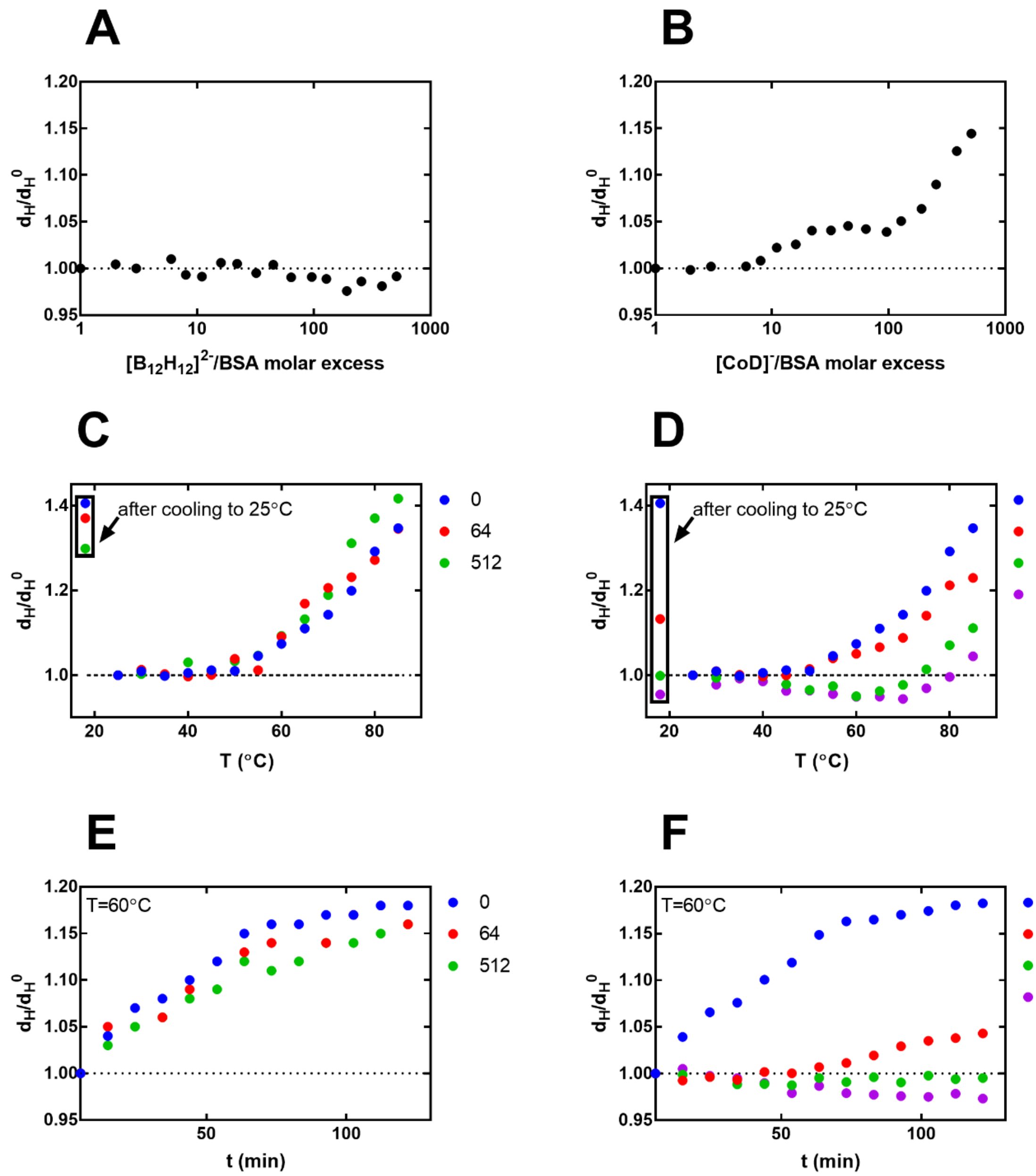

Figure S5. Relative hydrodynamic diameter of BSA determined by the DLS method: as a function of concentration of $[B_{12}H_{12}]^{2-}$ (A) and $[CoD]^-$ (B), where d_H^0 is the hydrodynamic diameter of BSA without boron clusters addition, boron clusters concentration were in the range 0-7.7mM; as a function of temperature with specified in the legend $[B_{12}H_{12}]^{2-}$/BSA (C) and $[CoD]^-$/BSA (D) molar ratio where d_H^0 is the hydrodynamic diameter of BSA with or without boron cluster in 25°C; as a function of time (kinetics of thermal denaturation of BSA)) at 60°C with specified in the legend $[B_{12}H_{12}]^{2-}$/BSA (E) and $[CoD]^-$/BSA (F) molar ratio, where d_H^0 is the initial value of hydrodynamic diameter of BSA with or without boron cluster (after 5min incubation at 60°C). All measurement were made in $NaHCO_3$ (0.1M) with constant concentration of BSA (15µM).

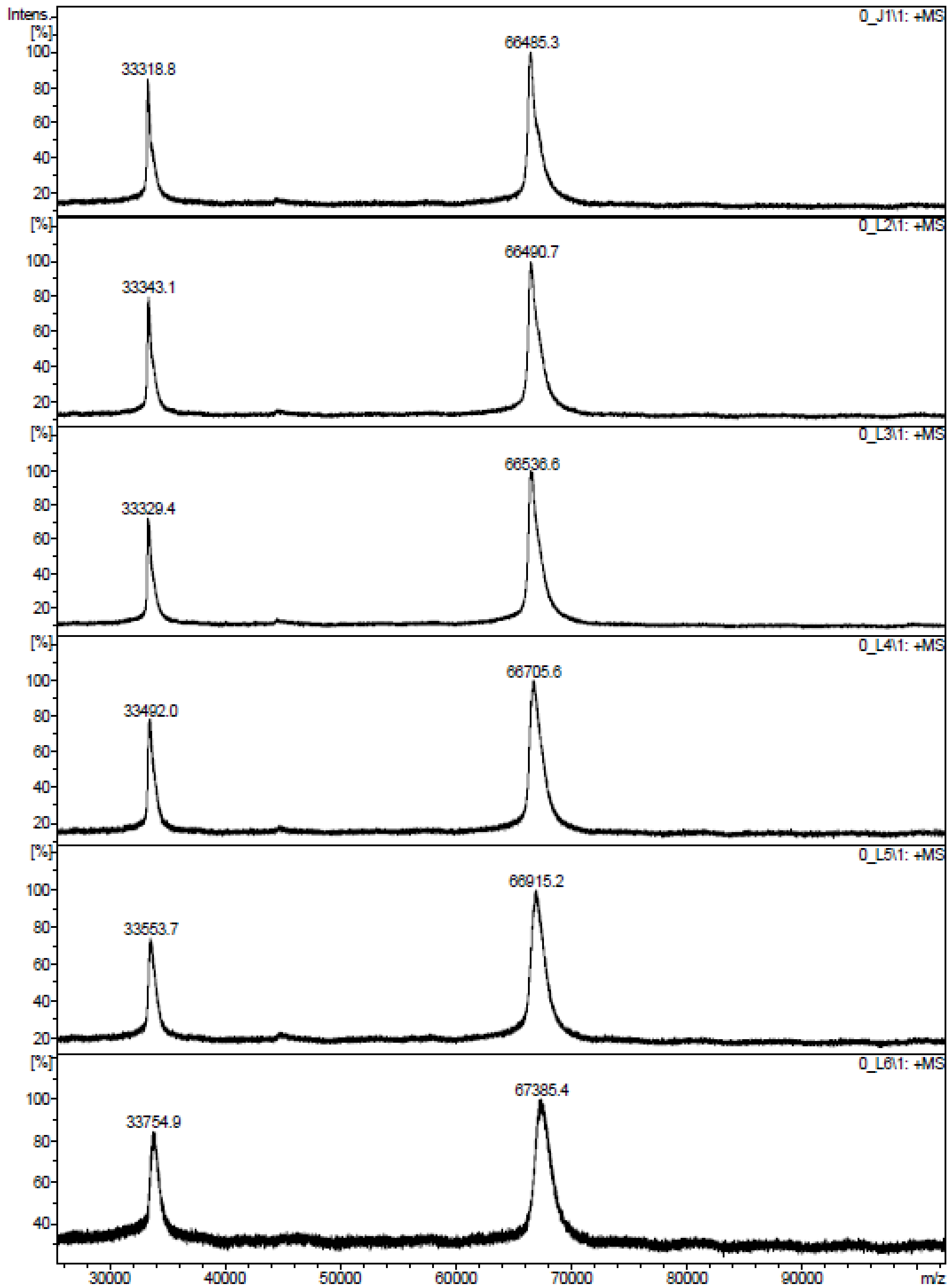

Figure S6. Linear positive MALDI mass spectra of nonconvalent binding complexes of BSA and $[B_{12}H_{12}]^{2-}$.

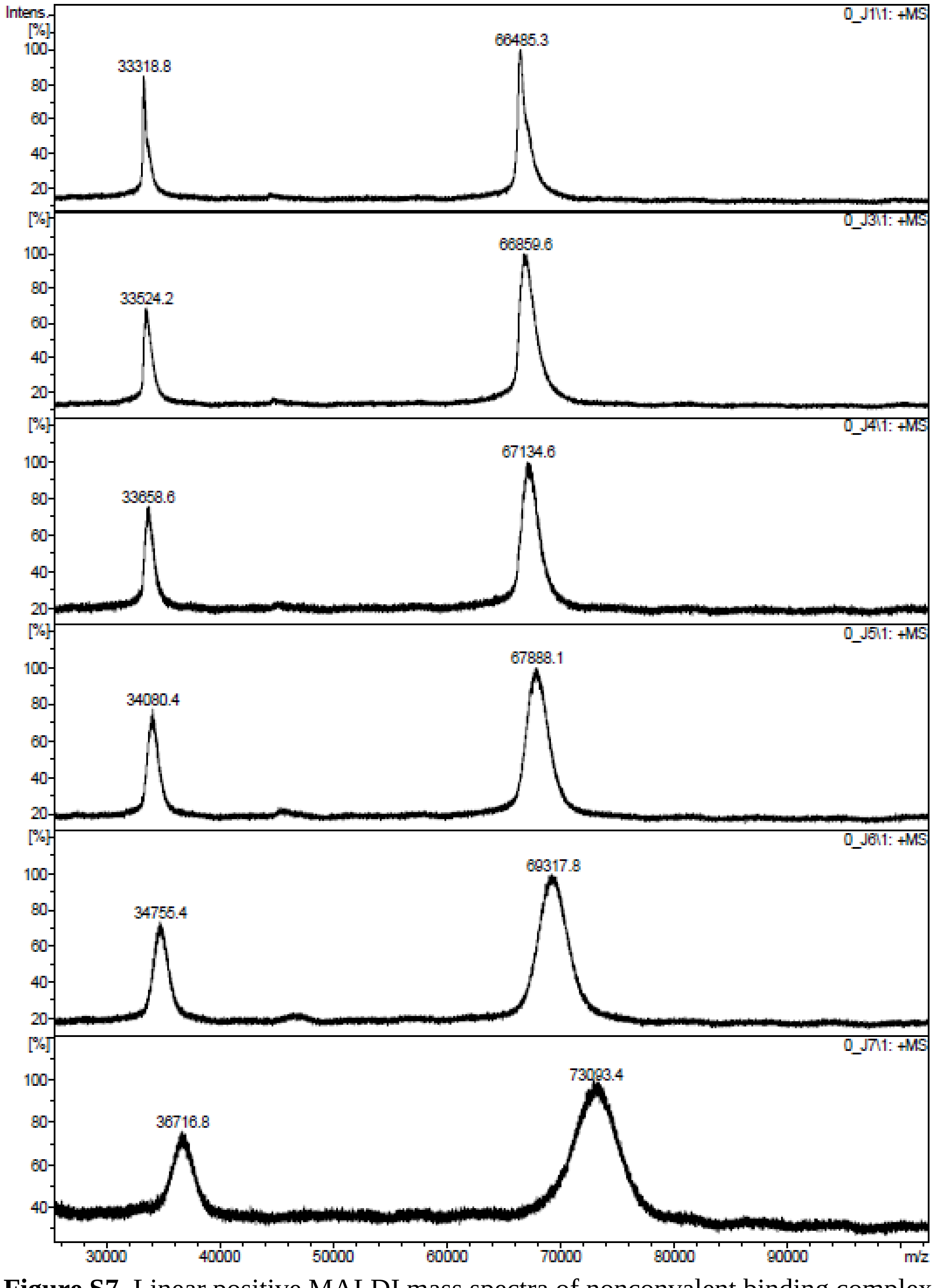

Figure S7. Linear positive MALDI mass spectra of nonconvalent binding complexes of BSA and $[CoD]^-$.

Table S1. Degree of quenching of: **1** – metallacarborane, **7** – *para*-carborane and **11** – dodecaborate. Fluorescence emission spectra for BSA (10.5 μM) in the presence of boron clusters in 0.10 M sodium bicarbonate (pH 8.4) with 2% DMSO was recorded from 300 to 500 nm, λ_{ex}=280 nm, at 298 K. The concentration of boron clusters was 10.5 μM. Equation for calculation of degree of quenching parameter, where F and F_0 are the steady-state fluorescence intensities in the presence and absence of quencher.

Compound	Degree of quenching [%]	Equation
1	60	
7	6	$degree\ of\ quenching = (1 - \frac{F}{F_0}) \cdot 100\%$
11	0	

Table S2. Stern-Volmer constant (K_{SV}) and quenching constant (k_q) for interaction of boron clusters (**1** to **11**) with BSA at 298, 304 and 310 K. Fluorescence emission spectra of BSA (10.5 μM) in the presence of boron clusters (**1** to **11**) in 0.10 M sodium bicarbonate(pH 8.4) with 2% DMSO, at λ_{ex}=280 nm was recorded. The concentration of **1** to **6** was 0 to 10.5 μM with 1.05 μM intervals; the concentration of **7** to **11** was 0 to 105 μM with 17.5 μM intervals.

Compund	T (K)	K_{SV} (M^{-1})	k_q (M^{-1} s^{-1})	r^2
1	298	$(1.51 \pm 0.07) \times 10^5$	2.51×10^{13}	0.9838
	304	$(1.54 \pm 0.07) \times 10^5$	2.57×10^{13}	0.9831
	310	$(1.60 \pm 0.07) \times 10^5$	2.67×10^{13}	0.9841
2	298	$(1.33 \pm 0.07) \times 10^5$	2.22×10^{13}	0.9808
	304	$(1.39 \pm 0.07) \times 10^5$	2.31×10^{13}	0.9812
	310	$(1.42 \pm 0.07) \times 10^5$	2.37×10^{13}	0.9828
3	298	$(9.19 \pm 0.37) \times 10^4$	1.53×10^{13}	0.9874
	304	$(9.30 \pm 0.40) \times 10^4$	1.55×10^{13}	0.9856
	310	$(9.34 \pm 0.43) \times 10^4$	1.56×10^{13}	0.9836
4	298	$(4.16 \pm 0.10) \times 10^4$	6.94×10^{12}	0.9953
	304	$(4.28 \pm 0.12) \times 10^4$	7.14×10^{12}	0.9942
	310	$(4.32 \pm 0.10) \times 10^4$	7.19×10^{12}	0.9959
5	298	$(1.13 \pm 0.04) \times 10^5$	1.88×10^{13}	0.9880
	304	$(1.17 \pm 0.05) \times 10^5$	1.94×10^{13}	0.9875
	310	$(1.20 \pm 0.05) \times 10^5$	2.00×10^{13}	0.9878
6	298	$(6.48 \pm 0.21) \times 10^4$	1.08×10^{13}	0.9915
	304	$(6.62 \pm 0.23) \times 10^4$	1.10×10^{13}	0.9906
	310	$(6.79 \pm 0.23) \times 10^4$	1.13×10^{13}	0.9911
7 - 11	298			
	304	n.d.		
	310			

Table S3. Binding parameters (binding constant – K_b and binding sites – n) and thermodynamic parameters (Gibbs free energy - ΔG^0, enthalpy - ΔH^0 and entropy - ΔS^0) for interaction of boron clusters (**1** to **11**) with BSA at 298, 304 and 310 K. Fluorescence emission spectra of BSA (10.5 µM) in the presence of boron clusters (**1** to **11**) in 0.10 M sodium bicarbonate (pH 8.4) with 2% DMSO, at λ_{ex}=280 nm was recorded. The concentration of **1** to **6** was 0 to 10.5 µM with 1.05 µM intervals; the concentration of **7** to **11** was 0 to 105 µM with 17.5 µM intervals.

	T (K)	logK_b	n	r^2	K_b (M^{-1})	$\Delta G^0{}_1$[a] (kJ mol^{-1})	$\Delta G^0{}_2$[b] (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
1	298	5.96 ± 0.21	1.17 ± 0.04	0.9906	9.11×10^5	-34.0	-34.0	31.8	221
	304	6.05 ± 0.21	1.19 ± 0.04	0.9910	1.13×10^6	-35.3	-35.2		
	310	6.18 ± 0.21	1.21 ± 0.04	0.9918	1.50×10^6	-36.6	-36.6		
2	298	5.51 ± 0.25	1.09 ± 0.05	0.9853	3.26×10^5	-31.4	-31.4	36.3	227
	304	5.63 ± 0.23	1.11 ± 0.04	0.9885	4.24×10^5	-32.8	-32.8		
	310	5.76 ± 0.20	1.13 ± 0.04	0.9910	5.75×10^5	-34.2	-34.2		
3	298	5.41 ± 0.18	1.10 ± 0.03	0.9927	2.56×10^5	-30.9	-30.9	35.2	222
	304	5.55 ± 0.18	1.12 ± 0.03	0.9929	3.51×10^5	-32.2	-32.3		
	310	5.65 ± 0.17	1.14 ± 0.03	0.9941	4.44×10^5	-33.5	-33.5		
4	298	5.72 ± 0.14	1.22 ± 0.03	0.9966	5.21×10^5	-32.6	-32.6	32.6	219
	304	5.85 ± 0.16	1.25 ± 0.03	0.9955	7.00×10^5	-34.0	-34.0		
	310	5.94 ± 0.15	1.26 ± 0.03	0.9959	8.67×10^5	-35.3	-35.2		
5	298	5.76 ± 0.20	1.15 ± 0.04	0.9919	5.70×10^5	-32.8	-32.8	30.0	211
	304	5.85 ± 0.19	1.17 ± 0.04	0.9926	7.06×10^5	-34.1	-34.0		
	310	5.96 ± 0.17	1.19 ± 0.03	0.9945	9.11×10^5	-35.4	-35.4		
6	298	5.21 ± 0.11	1.08 ± 0.02	0.9970	1.61×10^5	-29.7	-29.7	41.1	238
	304	5.37 ± 0.13	1.12 ± 0.02	0.9960	2.33×10^5	-31.2	-31.2		
	310	5.49 ± 0.12	1.14 ± 0.02	0.9967	3.06×10^5	-32.6	-32.6		
7-11	298								
	304	n.d.							
	310								

[a] $\Delta G_1 = \Delta H - T\Delta S$

[b] $\Delta G_2 = \mathrm{RTln}(K_b)$