ELECTRONIC SUPPLEMENTARY MATERIAL

ML and ML_2 Complexes Forming Between Ca(II) and D-glucose Derivatives in Aqueous Solutions

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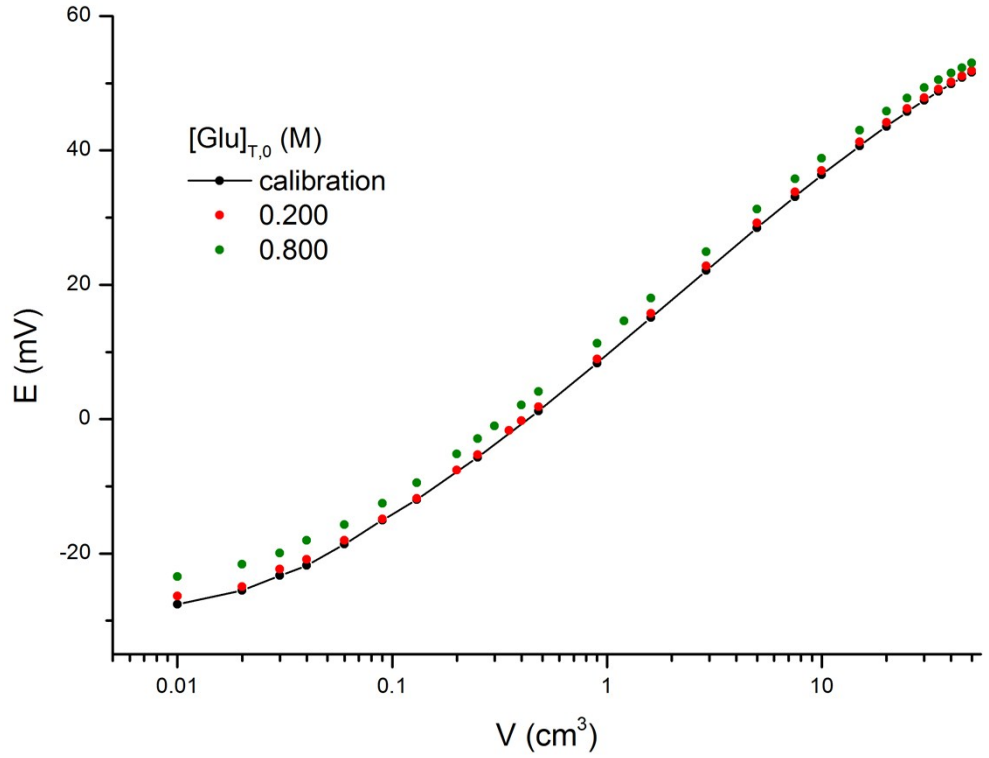

Fig. S1 Ca-ISE titration curves for the system containing glucose (Glu). (Y axis: measured cell potential; X axis: the volume of the added titrant on a logarithmic scale.) Initial $[Ca^{2+}]_T = 10^{-4}$ M; titrant concentration: $[CaCl_2]_T = 0.2$ M; initial volume: 70 cm^3. T = 25 °C, I = 1 M. For better visualization, the calibration points are linked with black solid line.

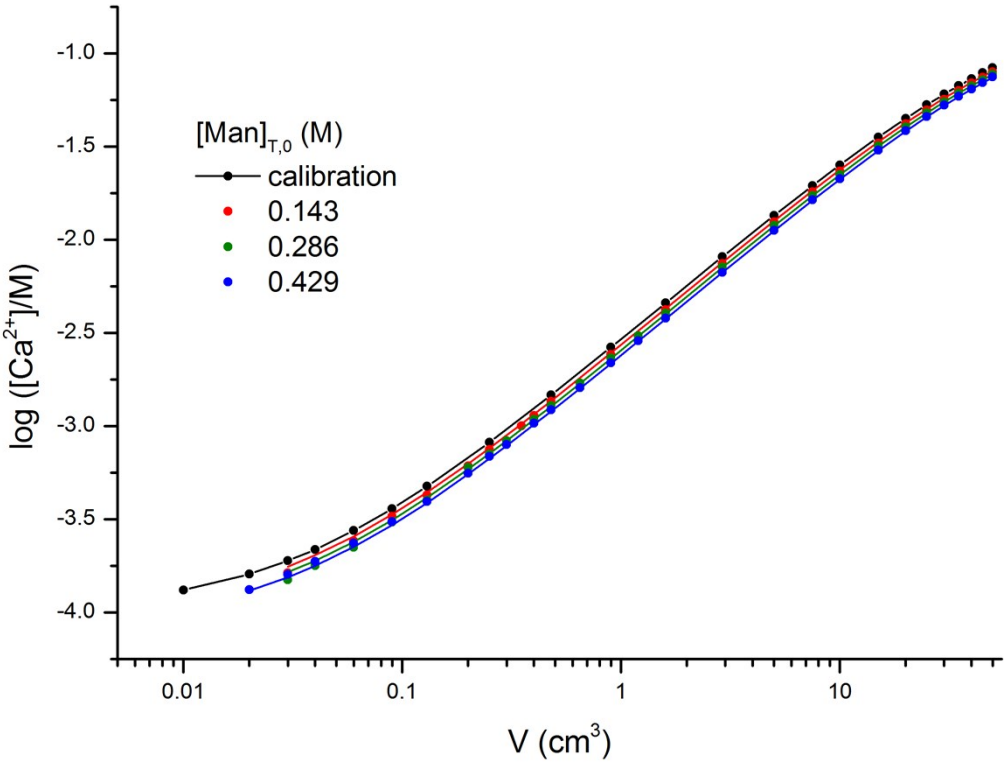

Fig. S2 Ca-ISE titration curves for the system containing mannitol (Man). (Y axis: logarithm of the free calcium ion concentration, $[Ca^{2+}]$; X axis: the volume of the added titrant on a logarithmic scale.) Initial

$[Ca^{2+}]_T = 10^{-4}$ M; titrant concentration: $[CaCl_2]_T = 0.2$ M; initial volume: 70 cm^3. T = 25 °C, I = 1 M. Symbols represent the measured, while solid lines represent the calculated points assuming the formation of the $CaMan^{2+}$ complex ($\log K_{1,1} = -0.28$). For better visualization, the calibration points are linked with solid line.

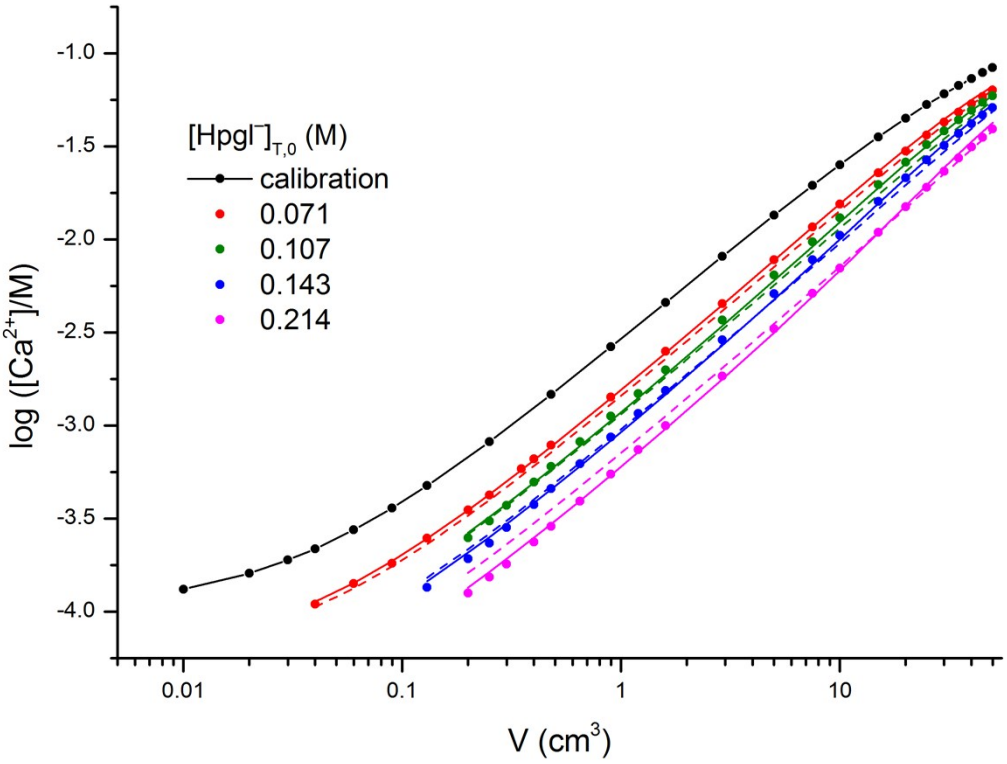

Fig. S3 Ca-ISE titration curves for for the system containing heptagluconate ($Hpgl^-$). (Y axis: logarithm of the free calcium ion concentration, $[Ca^{2+}]$; X axis: the volume of the added titrant on a logarithmic scale.) Initial $[Ca^{2+}]_T = 10^{-4}$ M; titrant concentration: $[CaCl_2]_T = 0.2$ M; initial volume: 70 cm^3. T = 25 °C, I = 1 M. Symbols represent the measured points. Dashed lines: calculated assuming the formation of the $CaHpgl^+$ complex ($\log K_{1,1} = 1.17$); solid lines: calculated assuming the formation of the $CaHpgl^+$ and $CaHpgl_2^0$ complexes ($\log K_{1,1} = 1.00$ and $\log \beta_{1,2} = 1.61$). For better visualization, the calibration points are linked with solid line.

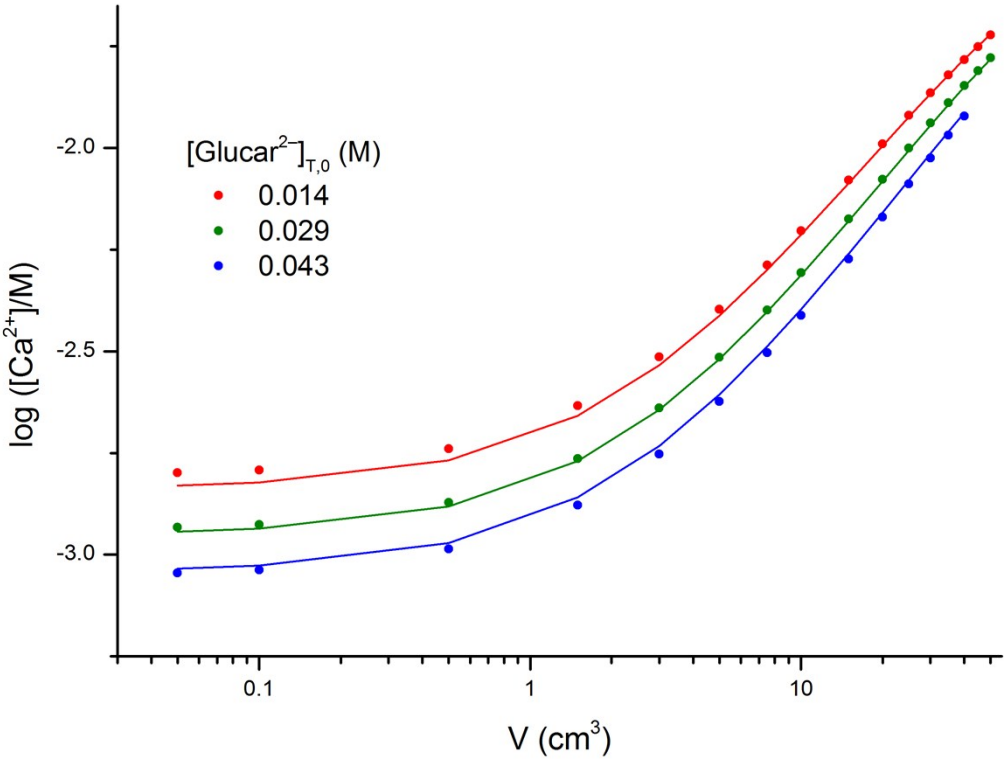

Fig. S4 Ca-ISE titration curves for for the system containing glucarate ($Glucar^{2-}$). (Y axis: logarithm of the free calcium ion concentration, $[Ca^{2+}]$; X axis: the volume of the added titrant on a logarithmic scale.) Initial $[Ca^{2+}]_T = 10^{-4}$ M (calibration) and $2 \cdot 10^{-3}$ M (measurements); titrant concentration: $[CaCl_2]_T = 0.05$ M; initial volume: 70 cm^3. T = 25 °C, I = 1 M. Symbols represent the measured points, while solid lines represent the calculated points assuming the formation of the $CaGlucar^0$ complex ($\log K_{1,1} = 1.48$).

Table S1 Freezing-point depression measurements for the system containing various amounts of $CaCl_2$, NaHpgl or $CaHpgl_2$. $\Delta\Delta T_f$ means the difference between the theoretical ($\Delta T_{f,theo}$, can be calculated by assuming complete dissocation of each compounds) and measured ($\Delta T_{f,meas}$) freezing-point depression. This term is the measure of the decrease in the overall concentration.

$[NaHpgl]_T$ (M)	$[CaCl_2]_T$ (M)	$[CaHpgl_2]_T$ (M)	$\Delta T_{f,theo}$ (°C)	$\Delta T_{f,meas}$ (°C)	$\Delta\Delta T_f$ (°C)
0.100	0	0	0.37	0.39	–0.02
0.200	0	0	0.74	0.75	–0.01
0.300	0	0	1.11	1.06	0.05
0	0.020	0	0.11	0.09	0.02
0	0.036	0	0.20	0.20	0.00
0	0.051	0	0.28	0.30	–0.02
0	0.076	0	0.42	0.40	0.02
0	0.102	0	0.56	0.55	0.01
0	0.152	0	0.85	0.81	0.04
0	0.203	0	1.13	1.07	0.06
0.100	0.020	0	0.48	0.47	0.01
0.100	0.036	0	0.57	0.55	0.02
0.100	0.051	0	0.65	0.55	0.10
0.100	0.076	0	0.79	0.69	0.10
0.100	0.102	0	0.93	0.77	0.16
0.200	0.020	0	0.85	0.80	0.05
0.200	0.036	0	0.94	0.83	0.11
0.200	0.051	0	1.02	0.90	0.12
0.200	0.076	0	1.16	0.99	0.17

0.200	0.102	0	1.30	1.10	0.20
0.300	0.102	0	1.67	1.28	0.39
0.300	0.152	0	1.96	1.51	0.45
0.300	0.203	0	2.24	1.71	0.53
0	0	0.020	0.11	0.06	0.05
0	0	0.040	0.22	0.16	0.06
0	0	0.080	0.44	0.27	0.17

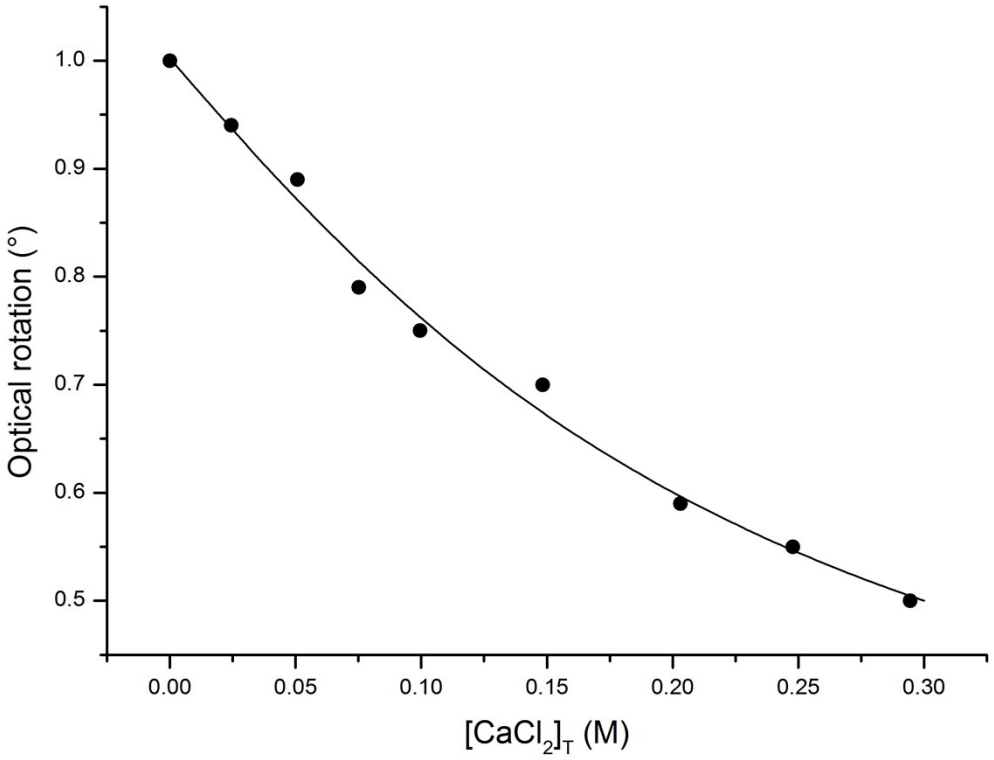

Fig. S5 Variation of the optical rotation of an aqueous solution containing $[NaGluc]_T$ = 0.200 M as a function of the added $CaCl_2$ concentration. Path length: 200 mm, T = (23 ± 2) °C, I = 1 M. Symbols represent the measured points, while solid lines represent the calculated points assuming the formation of the $CaGluc^+$ and $CaGluc_2^0$ complexes (log $K_{1,1}$ = 1.08 and log $\beta_{1,2}$ = 1.65).

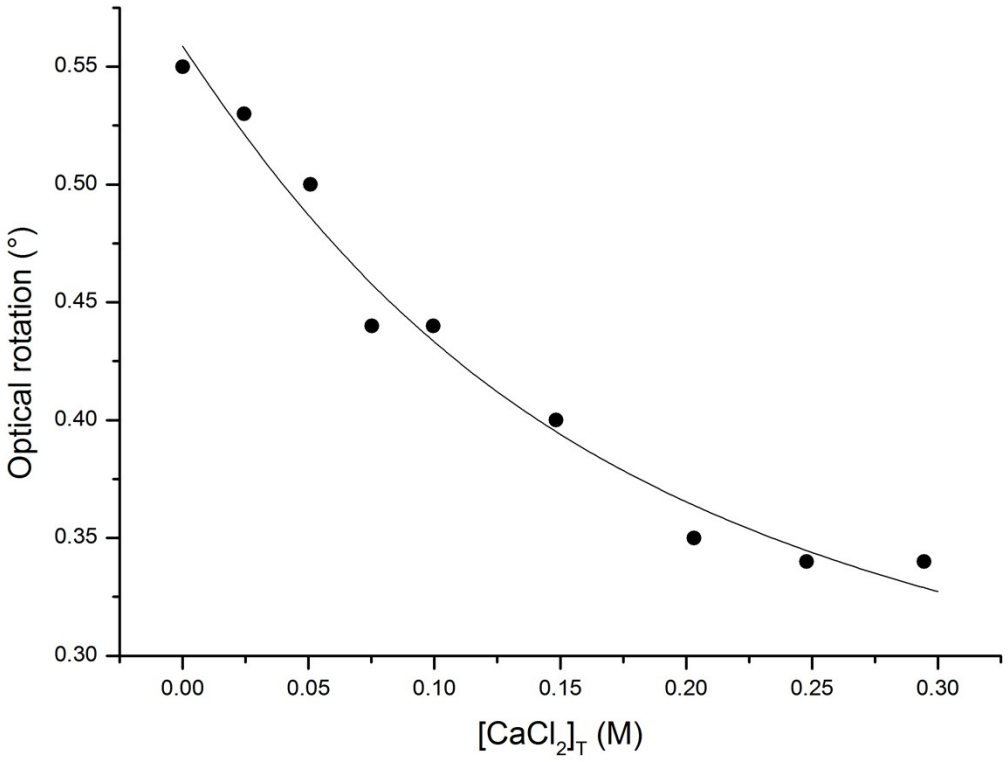

Fig. S6 Variation of the optical rotation of an aqueous solution containing $[NaHpgl]_T$ = 0.200 M as a function of the added $CaCl_2$ concentration. Path length: 200 mm, T = (23 ± 2) °C, I = 1 M. Symbols represent the measured points, while solid lines represent the calculated points assuming the formation of the $CaHpgl^+$ and $CaHpgl_2^0$ complexes (log $K_{1,1}$ = 1.00 and log $\beta_{1,2}$ = 1.61).