Supporting information

A new chiral ligand exchange capillary electrophoresis system based on Zn(II)-L-leucine complexes coordinating with β-cyclodextrin and its application in screening tyrosinase inhibitors

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CDs	Dns-D,L-Val				Dns-D,L-Tyr				Dns-D,L-Phe			
	Rs⁵	t∟/ min	t _D / min	N∟ ^c	Rs⁵	t _L /	t _D /	N∟ ^C plate m ⁻¹	Rs⁵	t∟/	t _D /	N∟ ^c
				plate m ⁻¹		min	min			min	min	plate m ⁻¹
α-CD	0.00	21.99	21.99	7562	0.00	25.52	25.52	8877	0.00	24.85	24.85	28247
β-CD	1.96	38.46	40.08	17533	1.84	47.60	49.44	30030	2.05	53.96	55.95	49615
γ-CD	3.87	42.11	47.09	37293	9.12	69.49	82.38	54053	6.85	94.77	109.72	62751

Table S1. Enantioseparation of Dns-D,L-AAs with different kinds of CDs^a

^a Running buffer: 100.0 mM boric acid, 5.0 mM NH₄ AC, 3.0 mM Zn(II), 6.0 mM L-Leu, adjusted pH to 8.2, and different kinds of CDs. Other conditions are the same as in **Figure S1**.

 $^{\rm b}$ Rs = 2(t_D-t_L)/(W_D + W_L); t: migration time

^cN: The number of theoretical plates



Fig. S1. A. Influence of β-CD concentration on migration times. Buffer conditions: 100.0 mM boric acid, 5.0 mM NH₄AC, 3.0 mM Zn(II), 6.0 mM L-Leu, adjusted pH to 8.2, and different concentrations of β-CD ranging from 0-5.0 mM. **B.** Influence of pH on migration times. Buffer conditions: 100.0 mM boric acid, 5.0 mM NH₄AC, 3.0 mM Zn(II), 6.0 mM L-Leu and 4.0 mM β-CD at different pH values. **C.** Influence of concentration ratio of Zn(II) to L-Leu on migration times. Buffer conditions: 100.0 mM boric acid, 5.0 mM NH₄AC, 4.0 mM β-CD, the concentration ratio of Zn(II) to L-Leu was from 2: 1 to 1:2.5 with Zn(II) kept at 3.0 mM, adjusted pH to 8.2. **D.** Influence of complex concentration on migration times. Buffer conditions: 100.0 mM NH₄AC, 4.0 mM β-CD and different to 8.2. **D.** Influence of 2.0-6.0 mM, the ratio of Zn(II) to L-Leu was kept at 1:2, adjusted pH to 8.2. Capillary: 60 cm, 45 cm effective × 75 µm id; injection: siphoned for 8 s at 15 cm; voltage: -21 KV; UV detection: 254 nm; temperature: 25 °C.



Fig. S2. Tuning the enatiomer migration order (EMO) of Dns- L-Tyr (2.76 mM) and Dns-D-Tyr (0.92 mM) by CLE-CE with varying the ratio of ligand L-Leu to D-Leu at (A) 6:0, (B) 3:3 and (C) 0:6. Other conditions were same as that in **Fig. 2**.

Dns-D,L-AAs	F	Running bu without β-0	ffer CD	Running buffer without Zn(II)-L-Leu complex				
	Rs⁵	t∟/min	t _D /min	Rs⁵	t∟/min	t _D /min		
Dns-D,L-Tyr	0	28.38	28.38	1.09	7.01	7.09		
Dns-D,L-Val	0	17.87	17.87	0	6.17	6.17		
Dns-D,L-Phe	0	14.99	14.99	0	6.52	6.52		

Table S2. Enantioseparation of Dns-D,L-AAs with different running buffer^a

^a Running buffer: 100.0 mM boric acid, 5.0 mM NH₄ AC without β -CD or without Zn(II)-L-Leu complex at pH 8.2. Other conditions are the same as in **Figure S1**.

 $^{\rm b}$ Rs = 2(t_D-t_L)/(W_D + W_L); t: migration time



Fig. S3. Lineweaver–Burk plot for the oxidation of L-Tyr catalyzed by tyrosinase (565 U/mg) with the concentrations of L-Tyr varied from 111 to 275 μ M. The Michaelis–Menten equation was described as: v=V_{max} [S] / (K_m+[S]), where [S] is the concentration of the substrate.



Fig. S4. Tyrosinase inhibition efficiency of different inhibitors: (A) 4-HC; (B) 4'-HC; (C) 2'-HC; (D) Chalcone; (E) 2-HC. The insert graphs represent the linear plot. Incubation condition: 333 μ M L-Tyr as the substrate and the selected five inhibitors in different concentrations were incubated with tyrosinase for 15 min at 25 °C.