<Electronic Supporting Information>

Self-assembly of Ni(II) with chiral ligand pair vs mixture of chiral ligand pair: structural features and recognition ability of Ni_2L_4 cages

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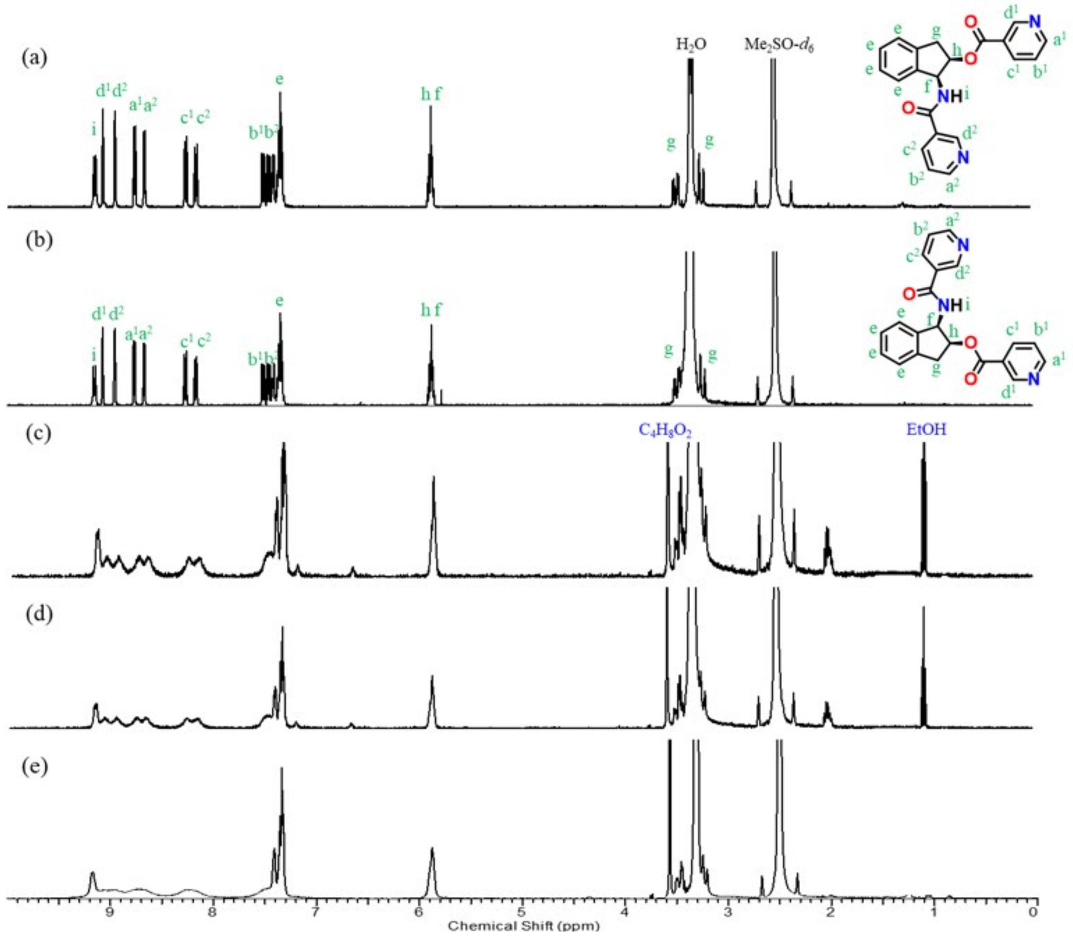

Fig. S1 ^{1}H NMR spectra (dissociated in Me_2SO-d_6) of *s,r*-L (a), *r,s*-L (b), $[2Cl@Ni_2Cl_2$(*s,r*-L)$_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot$EtOH (c), $[2Cl@Ni_2Cl_2$(*r,s*-L)$_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot$EtOH (d), and $[2Cl\cdot 2H_2O@Ni_2Cl_2$(*s,r*-L)$_2$(*r,s*-L)$_2(H_2O)_2]\cdot 7C_4H_8O_2$ (e).

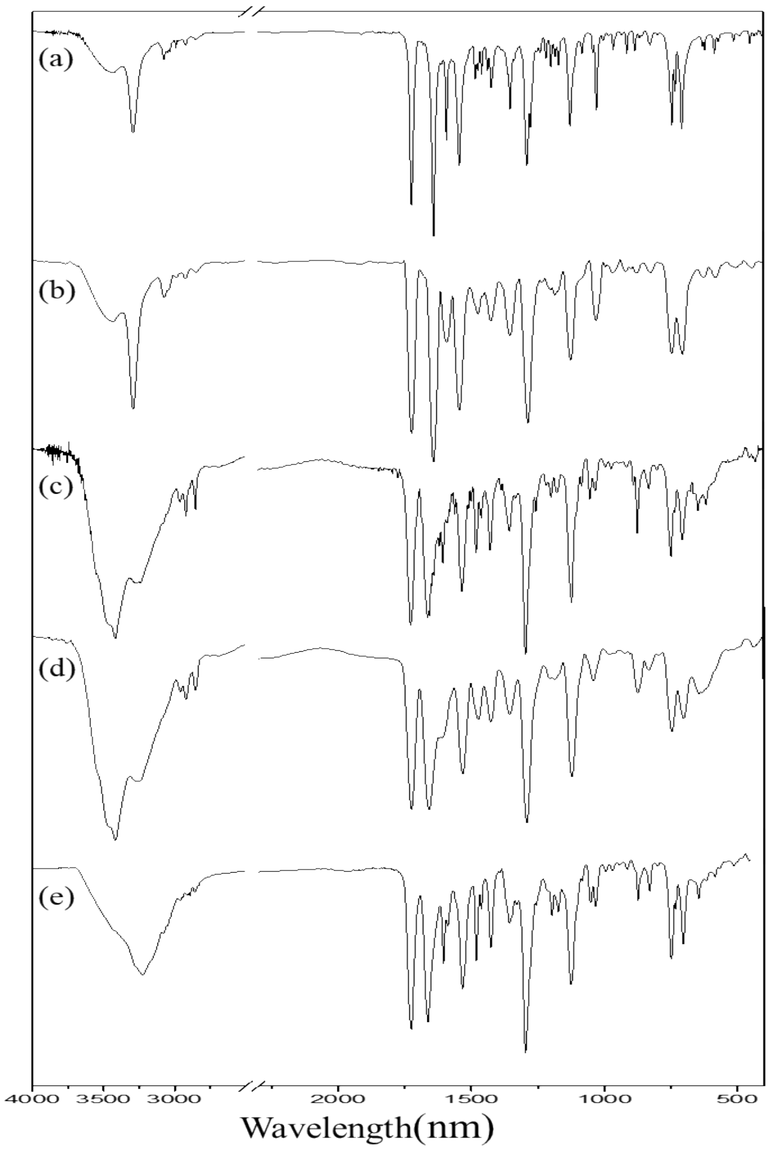

Fig. S2 IR spectra of *s*,*r*-L (a), *r*,*s*-L (b), [2Cl@Ni_2Cl_2(*s,r*-L)$_4$(H_2O)$_2$]·$4C_4H_8O_2$·EtOH (c), [2Cl@Ni_2Cl_2(*r,s*-L)$_4$(H_2O)$_2$]·$4C_4H_8O_2$·EtOH (d), and [2Cl·$2H_2O$@Ni_2Cl_2(*s,r*-L)$_2$(*r,s*-L)$_2$(H_2O)$_2$]·$7C_4H_8O_2$ (e).

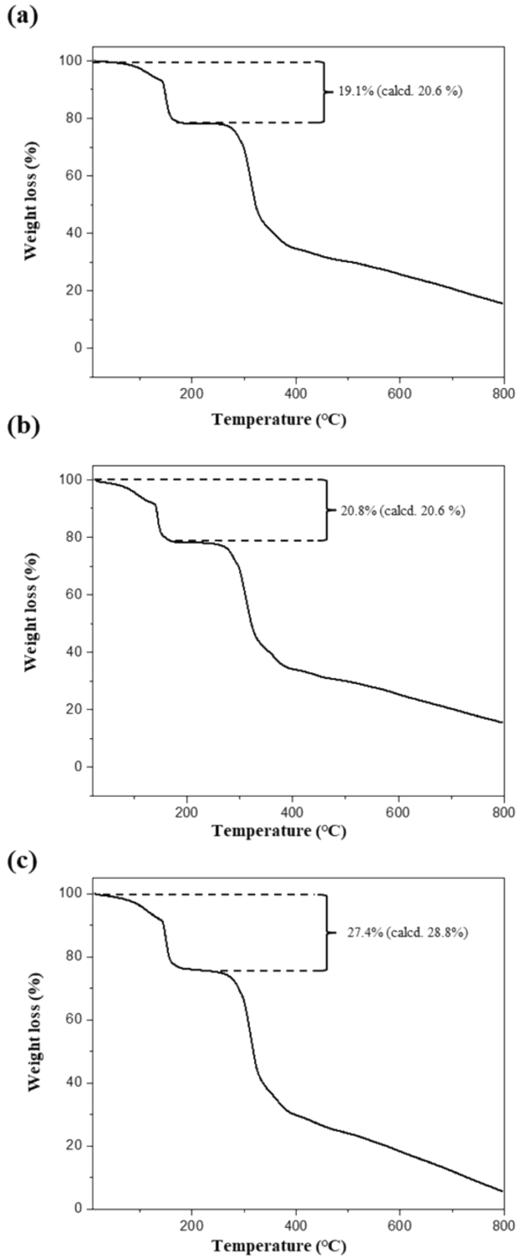

Fig. S3 TG curves of $[2Cl@Ni_2Cl_2(s,r\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ (a), $[2Cl@Ni_2Cl_2(r,s\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ (b), and $[2Cl\cdot 2H_2O@Ni_2Cl_2(s,r\text{-}L)_2(r,s\text{-}L)_2(H_2O)_2]\cdot 7C_4H_8O_2$ (c).

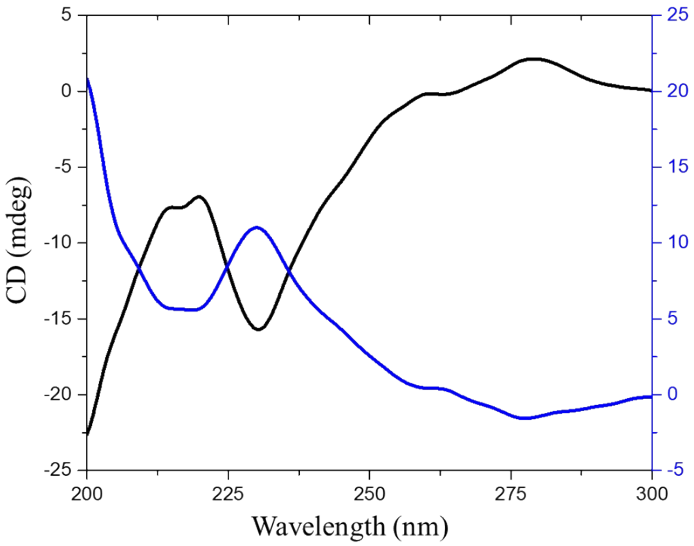

Fig. S4 CD spectra for *s,r*-L (black line) and *r,s*-L (blue line) in MeOH.

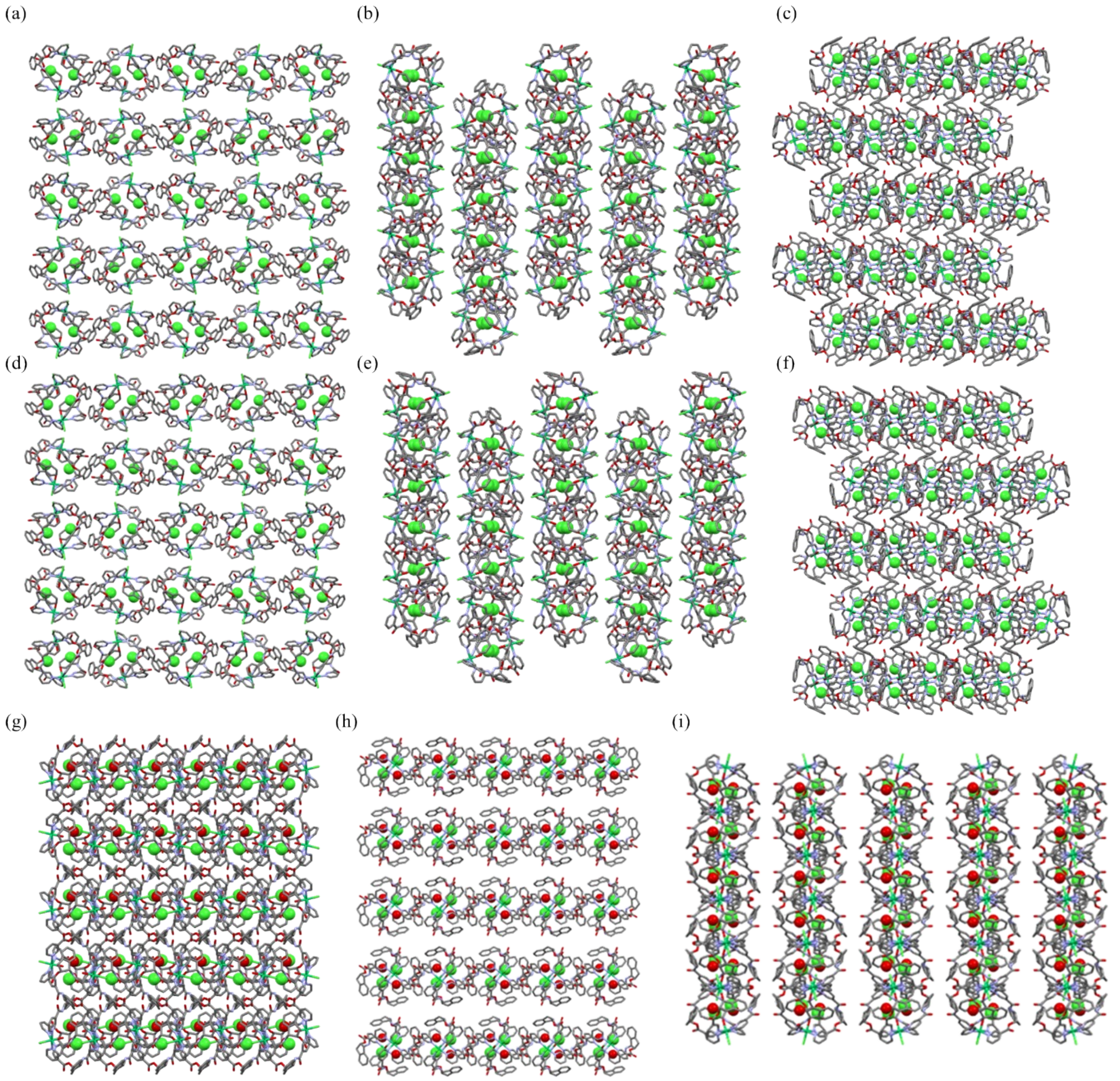

Fig. S5 Packing structures of $[2Cl@Ni_2Cl_2(s,r\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ in a axis (a), b axis (b), c axis (c), $[2Cl@Ni_2Cl_2(r,s\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ in a axis (d), b axis (e), c axis (f), and $[2Cl\cdot 2H_2O@Ni_2Cl_2(s,r\text{-}L)_2(r,s\text{-}L)_2(H_2O)_2]\cdot 7C_4H_8O_2$ in a axis (g), b axis (h) and c axis (i).

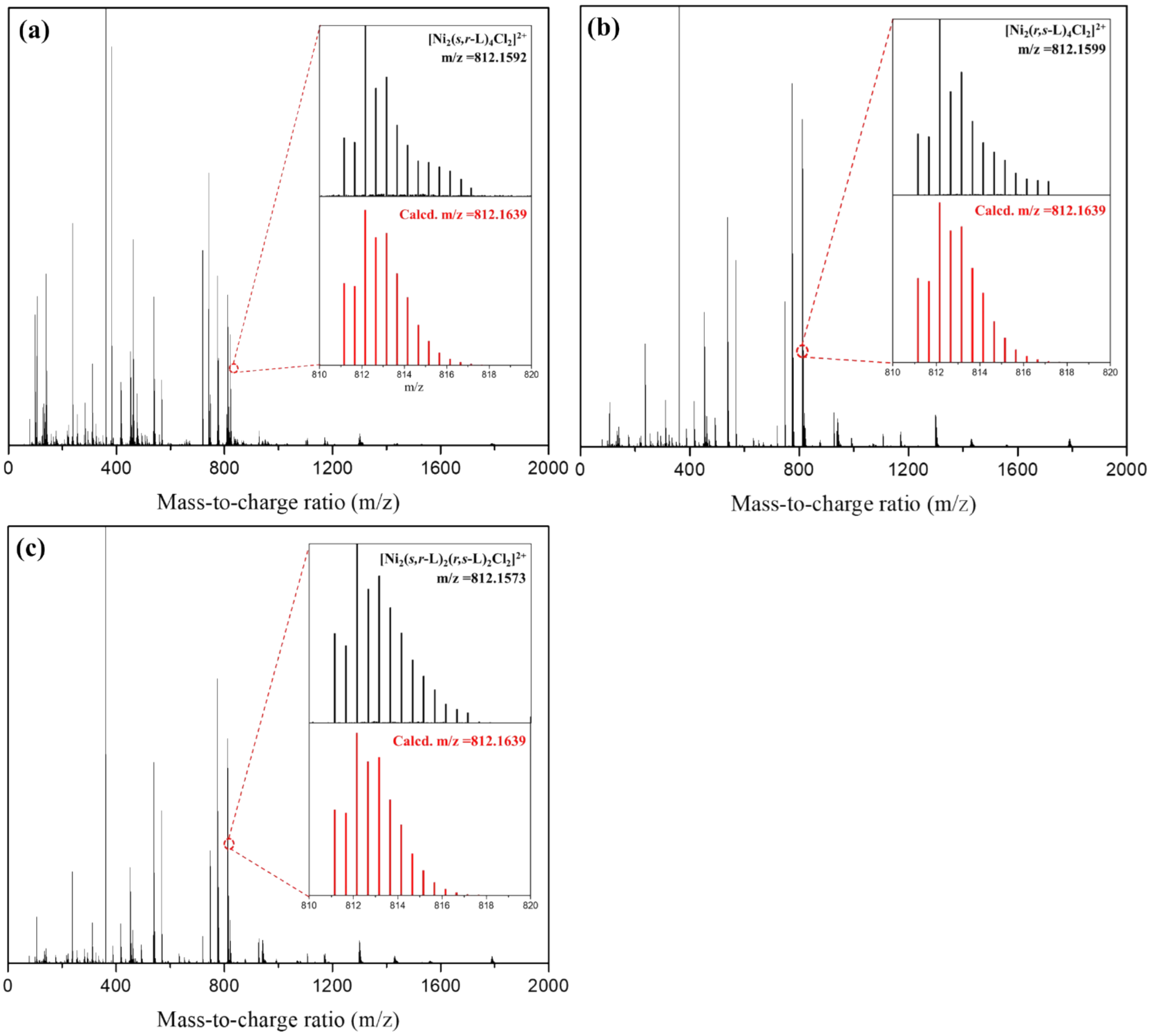

Fig. S6 ESI-mass fragments of $[2Cl@Ni_2Cl_2(\textit{s,r}\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ (a), $[2Cl@Ni_2Cl_2(\textit{r,s}\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ (b), and $[2Cl\cdot 2H_2O@Ni_2Cl_2(\textit{s,r}\text{-}L)_2(\textit{r,s}\text{-}L)_2(H_2O)_2]\cdot 7C_4H_8O_2$ (c).

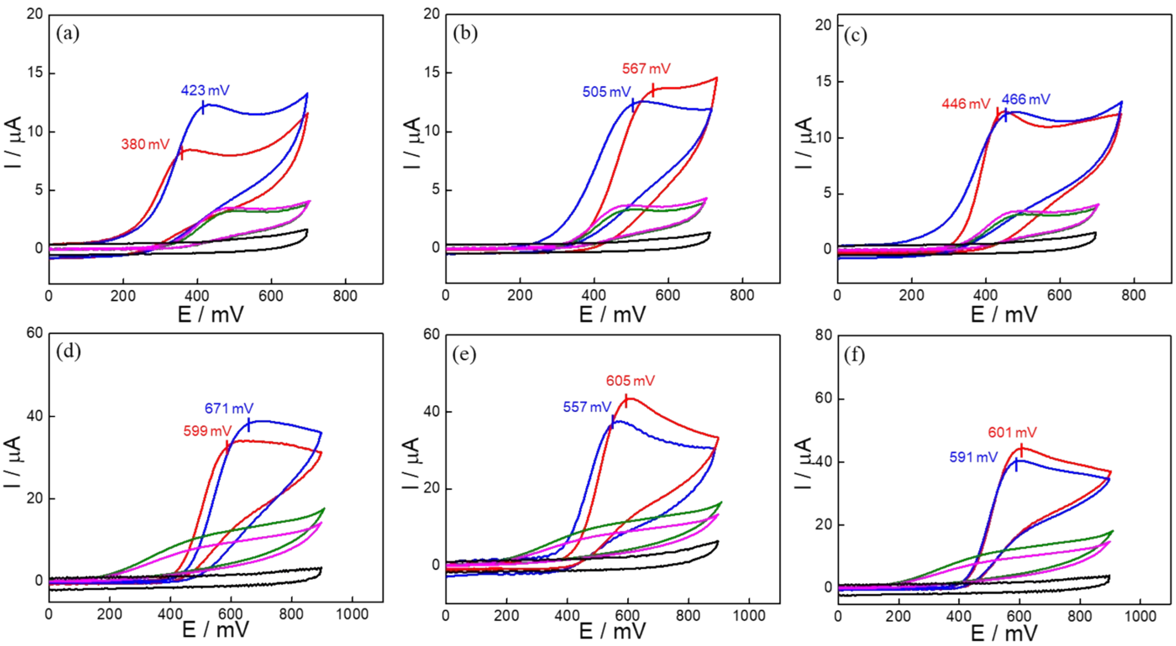

Fig. S7 Cyclic voltammetry (CV) signals of *l*-tryptophan only (green line), *d*-tryptophan only (pink line), the cage (black line) and that cage in presence of 1.0 mM *l*-tryptophan (blue line) and *d*-tryptophan (red line). $[2Cl@Ni_2Cl_2(s,r\text{-}L)_4(H_2O)_2]\cdot4C_4H_8O_2\cdot EtOH$ (a); $[2Cl@Ni_2Cl_2(r,s\text{-}L)4(H_2O)_2]\cdot4C_4H_8O_2\cdot EtOH$ (b); $[2Cl\cdot2H_2O@Ni_2Cl_2(r,s\text{-}L)_2(s,r\text{-}L)_2(H_2O)_2]\cdot7C_4H_8O_2$ (c). Cyclic voltammetry (CV) signals of *l*-cysteine only (green line), *d*-cysteine only (pink line), the cage (black line) and that cage in presence of 1.0 mM *l*-cysteine (blue line) and *d*-cysteine (red line). $[2Cl@Ni_2Cl_2(s,r\text{-}L)_4(H_2O)_2]\cdot4C_4H_8O_2\cdot EtOH$ (d); $[2Cl@Ni_2Cl_2(r,s\text{-}L)4(H_2O)_2]\cdot4C_4H_8O_2\cdot EtOH$ (e); $[2Cl\cdot2H_2O@Ni_2Cl_2(r,s\text{-}L)_2(s,r\text{-}L)_2(H_2O)_2]\cdot7C_4H_8O_2$ (f).

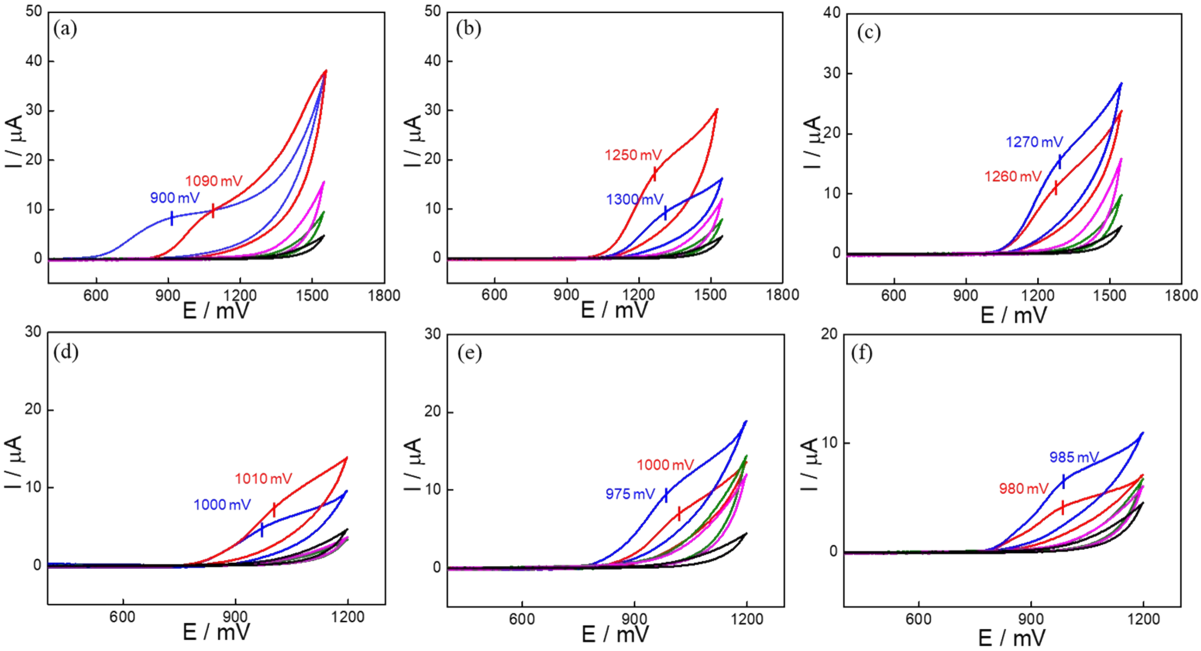

Fig. S8 Cyclic voltammetry (CV) signals of *l*-histidine only (green line), *d*-histidine only (pink line), the cage (black line) and that cage in presence of 1.0 mM *l*-histidine (blue line) and *d*-histidine (red line). [2Cl@Ni_2Cl_2(*s,r*-L)$_4$(H_2O)$_2$]·$4C_4H_8O_2$·EtOH (a); [2Cl@Ni_2Cl_2(*r,s*-L)4(H_2O)$_2$]·$4C_4H_8O_2$·EtOH (b); [2Cl·$2H_2O$@Ni_2Cl_2(*r,s*-L)$_2$(*s,r*-L)$_2$(H_2O)$_2$]·$7C_4H_8O_2$ (c). Cyclic voltammetry (CV) signals of *l*-phenylalanine only (green line), *d*-phenylalanine only (pink line), the cage (black line) and that cage in presence of 1.0 mM *l*-phenylalanine (blue line) and *d*-phenylalanine (red line). [2Cl@Ni_2Cl_2(*s,r*-L)$_4$(H_2O)$_2$]·$4C_4H_8O_2$·EtOH (d); [2Cl@Ni_2Cl_2(*r,s*-L)4(H_2O)$_2$]·$4C_4H_8O_2$·EtOH (e); [2Cl·$2H_2O$@Ni_2Cl_2(*r,s*-L)$_2$(*s,r*-L)$_2$(H_2O)$_2$]·$7C_4H_8O_2$ (f).

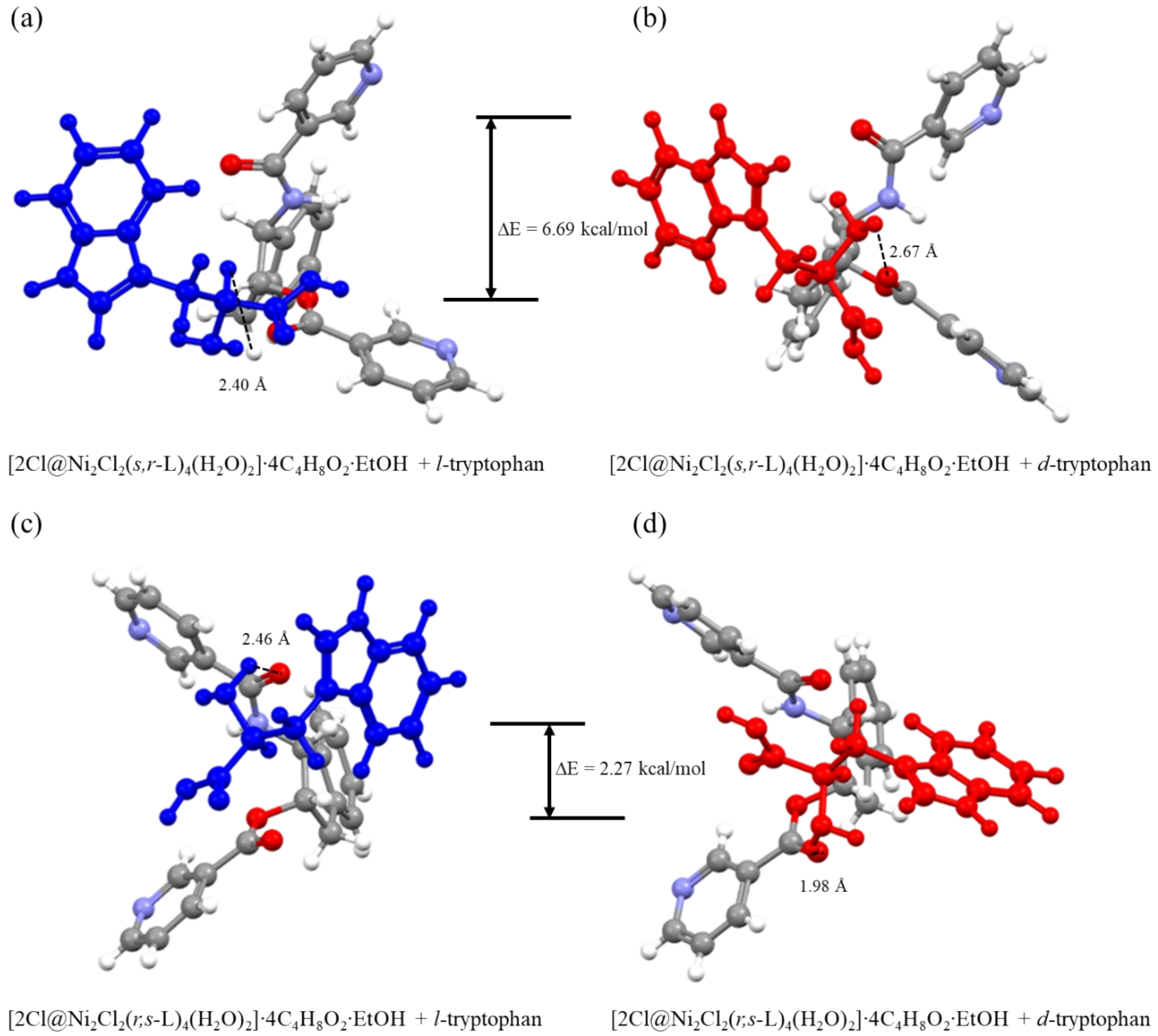

Fig. S9 Computational simulation of ligand moiety of chiral cages and tryptophan via MM2 calculation: $[2Cl@Ni_2Cl_2(s,r\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ with *l*-tryptophan (a), $[2Cl@Ni_2Cl_2(s,r\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ with *d*-tryptophan (b), $[2Cl@Ni_2Cl_2(r,s\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ with *l*-tryptophan (c), and $[2Cl@Ni_2Cl_2(r,s\text{-}L)_4(H_2O)_2]\cdot 4C_4H_8O_2\cdot EtOH$ + *d*-tryptophan (d). The energy differences had been calculated by Chem3D with MM2 method.

Table S1 Crystallographic data.

	[2Cl@Ni_2Cl_2(*s*,*r*-L)$_4$ (H_2O)$_2$]·4$C_4H_8O_2$·EtOH	[2Cl@Ni_2Cl_2(*r*,*s*-L)$_4$ (H_2O)$_2$]·4$C_4H_8O_2$·EtOH	[2Cl·2H_2O@Ni_2Cl_2(*r*,*s*-L)$_2$ (*s*,*r*-L)$_2$(H_2O)$_2$]·7$C_4H_8O_2$
Formula	$C_{102}H_{110}N_{12}O_{23}Ni_2Cl_4$	$C_{102}H_{110}N_{12}O_{23}Ni_2Cl_4$	$C_{112}H_{132}N_{12}O_{30}Ni_2Cl_4$
M_w	2131.23	2131.23	2385.51
Cryst. sys.	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$C2/c$
a (Å)	14.855(3)	14.854(3)	30.615(6)
b (Å)	26.201(5)	26.201(5)	15.581(2)
c (Å)	26.599(5)	26.589(5)	23.797(4)
α (°)	-	-	-
β (°)	-	-	90.285(7)°
γ (°)	-	-	-
V (Å^3)	10353(4)	10348(4)	11351(3)
Z	4	4	4
ρ (g cm^{-3})	1.367	1.368	1.396
μ (mm^{-1})	0.519	0.426	0.509
R_{int}	0.1115	0.0540	0.1347
GoF on F^2	0.957	1.002	1.046
R_1 [I>2$\sigma(I)$][a]	0.0666	0.0624	0.1322
wR_2 (all data)[b]	0.1942	0.1926	0.4158

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b]$wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$

Table S2 Selected bond length (Å) and angle (º).

[2Cl@Ni_2Cl_2(*s*,*r*-L)$_4$ $(H_2O)_2$]·$4C_4H_8O_2$·EtOH		[2Cl@Ni_2Cl_2(*r*,*s*-L)$_4$ $(H_2O)_2$]·$4C_4H_8O_2$·EtOH		[2Cl·$2H_2O$@Ni_2Cl_2(*r*,*s*-L)$_2$ (*s*,*r*-L)$_2$$(H_2O)_2$]·$7C_4H_8O_2$	
Cl(1)-Ni(1)	2.386(1)	Cl(1)-Ni(1)	2.387(1)	Ni(1)-N(2A)	2.105(7)
O(1)-Ni(1)	2.060(3)	O(1)-Ni(1)	2.057(3)	Ni(1)-O(1)	2.106(5)
Ni(1)-N(2B)	2.117(4)	Ni(1)-N(2D)	2.111(3)	Ni(1)-N(11A)#1	2.115(7)
Ni(1)-N(2D)	2.117(4)	Ni(1)-N(2B)	2.112(3)	Ni(1)-N(2B)#1	2.118(7)
Ni(1)-N(2C)	2.133(4)	Ni(1)-N(2A)	2.131(3)	Ni(1)-N(11B)	2.138(7)
Ni(1)-N(2A)	2.135(4)	Ni(1)-N(2C)	2.132(3)	Ni(1)-Cl(1)	2.383(2)
O(1)-Ni(1)-N(2B)	89.8(2)	O(1)-Ni(1)-N(2D)	89.8(1)	N(2A)-Ni(1)-O(1)	90.4(2)
O(1)-Ni(1)-N(2D)	88.8(2)	O(1)-Ni(1)-N(2B)	88.7(1)	N(2A)-Ni(1)-N(11A)#1	176.6(3)
N(2B)-Ni(1)-N(2D)	178.1(2)	N(2D)-Ni(1)-N(2B)	178.1(1)	O(1)-Ni(1)-N(11A)#1	87.7(2)
O(1)-Ni(1)-N(2C)	92.2(1)	O(1)-Ni(1)-N(2A)	91.8(1)	N(2A)-Ni(1)-N(2B)#1	90.5(3)
N(2B)-Ni(1)-N(2C)	88.7(2)	N(2D)-Ni(1)-N(2A)	88.7(1)	O(1)-Ni(1)-N(2B)#1	86.2(2)
N(2D)-Ni(1)-N(2C)	90.1(2)	N(2B)-Ni(1)-N(2A)	90.2(1)	N(11A)#1-Ni(1)-N(2B)#1	92.1(3)
O(1)-Ni(1)-N(2A)	89.4(1)	O(1)-Ni(1)-N(2C)	89.8(1)	N(2A)-Ni(1)-N(11B)	86.7(3)
N(2B)-Ni(1)-N(2A)	91.4(2)	N(2D)-Ni(1)-N(2C)	91.4(1)	O(1)-Ni(1)-N(11B)	89.5(2)
N(2D)-Ni(1)-N(2A)	89.8(2)	N(2B)-Ni(1)-N(2C)	89.8(1)	N(11A)#1-Ni(1)-N(11B)	90.5(3)
N(2C)-Ni(1)-N(2A)	178.4(2)	N(2A)-Ni(1)-N(2C)	178.5(1)	N(2B)#1-Ni(1)-N(11B)	174.8(2)
O(1)-Ni(1)-Cl(1)	178.2(1)	O(1)-Ni(1)-Cl(1)	178.28(8)	N(2A)-Ni(1)-Cl(1)	91.7(2)
N(2B)-Ni(1)-Cl(1)	90.9(1)	N(2D)-Ni(1)-Cl(1)	90.89(8)	O(1)-Ni(1)-Cl(1)	176.6(2)
N(2D)-Ni(1)-Cl(1)	90.6(1)	N(2B)-Ni(1)-Cl(1)	90.61(9)	N(11A)#1-Ni(1)-Cl(1)	90.4(2)
N(2C)-Ni(1)-Cl(1)	89.5(1)	N(2A)-Ni(1)-Cl(1)	89.81(9)	N(2B)#1-Ni(1)-Cl(1)	91.1(2)
N(2A)-Ni(1)-Cl(1)	88.9(1)	N(2C)-Ni(1)-Cl(1)	88.66(9)	N(11B)-Ni(1)-Cl(1)	93.4(2)
				#1 -x+3/2,-y+1/2,-z+1	