Supplementary Information

Two-step modulation of ion recognition using a

bis(saloph)-macocyclic host having a 24-crown-8-like cavity

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Table of Contents

• Experimental	Pages S3
• Synthesis of H_4L^2 and L^2Ni_2 (Scheme S1)	S4-5
• ESI-TOF mass spectra of H_4L^2 and L^2Ni_2 (Fig. S1-S2)	S6-7
• Crystallographic data for L ² Ni ₂ (Table S1)	S8
• ¹ H NMR titration studies of L ² Ni ₂ with M(OTf) _n (NaOTf, KOTf, RbOTf, CsOTf, Ca(OTf) ₂ , Sr(OTf) ₂ , Ba(OTf) ₂) (Fig. S3-S9)	S9-15
• ESI-TOF mass spectra of L^2Ni_2 in the presence of M(OTf) _n (NaOTf, KOTf, RbOTf, CsOTf, Sr(OTf) ₂ , Ba(OTf) ₂) (Fig. S10-S15)	S16-21
• UV-Vis titration studies of L ² Ni ₂ with M(OTf) _n (KOTf, RbOTf, CsOTf, Sr(OTf) ₂ , Ba(OTf) ₂) (Fig. S16-S20)	S22-26
• ¹ H NMR titration studies of DB24C8 with M(OTf) _n (NaOTf, KOTf, RbOTf, CsOTf, Sr(OTf) ₂ , Ba(OTf) ₂) (Fig. S21-S26)	827-32
• ¹ H NMR titration studies of H ₄ L ² with M(OTf) _n (NaOTf, KOTf, RbOTf, CsOTf, Sr(OTf) ₂ , Ba(OTf) ₂) (Fig. S27-S32)	S32-38
• DFT calculations of $[L^2Ni^{II}_2 \bullet Cs]^+$ and $[L^2Ni^{I}_2 \bullet Cs]^-$ (Fig. S33)	S39
• References	S40

Experimental

Materials and methods

Reagents and solvents were purchased from commercial sources and used without further purification. ¹H NMR spectra were recorded on a JEOL JNM-ECS 400 (400 MHz). Chemical shifts were referenced with respect to tetramethylsilane (0 ppm) as an internal standard or solvent residual peak (¹H, 2.50 ppm for DMSO- d_6 ; ¹³C, 77.16 ppm for CDCl₃ and 39.52 ppm for DMSO- d_6). ESI-TOF mass spectra were recorded on a Bruker Daltonics micrOTOF II. The UV-visible absorption spectra were measured on a JACSO V-770 UV/VIS/NIR spectrophotometer equipped with a JASCO EHCS-760 temperature/stirring controller.

X-ray Crystallography

Intensity data were collected on a Bruker SMART APEX II diffractometer (with Cu K α radiation, $\lambda = 1.54178$ Å). The data were corrected for Lorentz and polarization factors and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods (SHELXD) and refined by full-matrix least squares on F^2 using SHELXL 97.¹ Crystallographic data for L²Ni₂ have been deposited with the Cambridge Crystallographic Data Centre under reference number CCDC 1541501. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK).

Synthesis of H₄L² and L²Ni₂

2-Allyloxy-3-hydroxybenzaldehyde $(1)^2$ was prepared according to the procedure previously reported. H₄L² and L²Ni₂ were synthesized as outlined in Scheme S1.



Scheme S1.

Synthesis of 2

Under nitrogen atmosphere, 1,2-bis(tosyloxy)ethane (1.50 g, 4.06 mmol) was added to a mixture of **1** (2.17 g, 12.2 mmol) and potassium carbonate (1.68 g, 12.2 mmol) in degassed acetonitrile (200 mL). The reaction mixture was stirred overnight under reflux and then water (100 mL) was added. The mixture was extracted with chloroform (30 mL × 3) and the combined organic extract was dried over anhydrous magnesium sulfate. After the solvent was evaporated, the crude product was purified by column chromatography on silica gel (AcOEt/Hexane = 1:9 - 1:3) to yield **2** (1.45 g, 3.79 mmol, 93%) as pale yellow solid. ¹H NMR (400 MHz, 293 K, CDCl₃) δ 10.44 (s, 2H), 7.48 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.23 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.02 (ddt, *J* = 17.0, 10.5, 6.2 Hz, 2H), 5.31 (dd, *J* = 17.0, 1.3 Hz, 2H). 5.22 (dd, *J* = 10.5, 1.3 Hz, 2H), 4.67 (d, *J* = 6.2 Hz, 4H), 4.46 (s, 4H). ¹³C NMR (100 MHz, 293 K, CDCl₃) δ 190.45, 152.09, 151.78, 133.10, 130.55, 124.37, 120.20, 119.89, 119.13, 75.42, 67.89. Anal. Calcd for C₂₂H₂₂O₆•0.2H₂O: C, 68.45; H, 5.85. Found: C, 68.49; H, 5.80.

Synthesis of 3

Under nitrogen atmosphere, formic acid (1.5 mL, 39.4 mmol) and triethylamine (5.2 mL, 37.4 mmol) were sequentially added to a mixture of **2** (578 mg, 1.51 mmol), palladium(II) acetate (37.4 mg, 0.17 mmol), and triphenylphosphine (184 mg, 0.70 mmol) in degassed aqueous ethanol (80%, 150 mL). The mixture was stirred overnight at room temperature. The reaction mixture was acidified (pH = 1) with HCl (1 M, 30 mL)

and extracted with chloroform (150 mL × 4). The combined organic extract was concentrated to dryness and the crude product was treated with water, collected on a filter, and washed with water to remove inorganic salts. The residue was suspended in ethyl acetate and concentrated to remove the residual water by azeotropic distillation. The resulting material was washed with chloroform to yield **3** (392 mg, 1.30 mmol, 86%) as colorless solid. ¹H NMR (400 MHz, 293 K, DMSO-*d*₆) δ 10.27 (s, 2H), 10.17 (br, 2H), 7.36 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.29 (dd, *J* = 7.9, 1.4 Hz, 2H), 6.93 (t, *J* = 7.9 Hz, 2H), 4.43 (s, 4H). ¹³C NMR (100 MHz, 293 K, DMSO-*d*₆) δ 192.19, 150.90, 147.32, 122.60, 120.85, 119.35, 119.26, 67.59. Anal. Calcd for C₁₆H₁₄O₆•0.2H₂O: C, 62.83; H, 4.75. Found: C, 62.67; H, 4.49.

Synthesis of H₄L²

Under nitrogen atmosphere, a degassed DMSO solution of 1,2-phenylenediamine (1 M, 400 μ L, 0.40 mmol) was added to a solution of **3** (121 mg, 0.40 mmol) in degassed DMSO (12 mL). The reaction mixture was left to stand overnight at room temperature. The reaction mixture was poured into water (120 mL) and extracted with chloroform (120 mL). The combined organic extract was concentrated to a minimal volume. Addition of hexane led to the precipitation, which was collected to yield H₄L² (139 mg, 0.19 mmol, 93%) as orange solid. ¹H NMR (400 MHz, 293 K, DMSO-*d*₆) δ 13.17 (s, 4H), 8.96 (s, 4H), 7.51-7.46 (m, 4H), 7.44-7.39 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 6.91 (t, *J* = 8.0 Hz, 4H), 4.36 (s. 8H). ESI-MS *m*/*z* 749.3 [H₄L²+H]⁺. Anal. Calcd for C₄₄H₃₆N₄O₈•DMSO: C, 66.81; H, 5.12; N, 6.78. Found: C, 66.84; H, 5.10; N. 6.48.

Synthesis of L²Ni₂

A methanol solution of nickel(II) acetate tetrahydrate (6.7 mM, 18 mL, 120 µmol) was added to a suspension of H_4L^2 (45.0 mg, 60 µmol) in chloroform (42 mL). The reaction mixture was left to stand overnight at room temperature. Addition of diethyl ether led to the precipitation, which was collected to yield L^2Ni_2 (38.7 mg, 45 µmol, 75%) as dark red solid. ¹H NMR (400 MHz, 293 K, DMSO-*d*₆) δ 8.92 (s, 4H), 8.18-8.14 (m, 4H), 7.36-7.32 (m, 4H), 7.30 (d, *J* = 7.8 Hz, 4H), 6.99 (d, *J* = 7.8 Hz, 4H), 6.58 (t, *J* = 7.8 Hz, 4H), 4.42 (s, 8H). ESI-MS *m/z* 861.1 [L^2Ni_2 +H]⁺. Anal. Calcd for C₄₄H₃₂N₄Ni₂O₈•3H₂O: C, 57.68; H, 4.18; N, 6.12. Found: C, 57.58; H, 4.06; N. 5.96.

ESI-TOF mass spectra of H_4L^2 and L^2Ni_2



Fig. S1. ESI-TOF mass spectrum of H_4L^2 .



Fig. S2. ESI-TOF mass spectrum of L²Ni₂.

Crystallographic data for L²Ni₂

	$[L^2Ni_2]$ •2CHCl ₃
Formula	C ₄₆ H ₃₄ Cl ₆ N ₄ Ni ₂ O ₈
Formula weight	1100.89
Temperature (K)	93
Crystal size (mm ³)	$0.14\times0.08\times0.07$
Crystal system	Orthorhombic
Space group	Cmcm
<i>a</i> (Å)	26.672(4)
<i>b</i> (Å)	7.4623(10)
<i>c</i> (Å)	21.658(3)
α (deg)	90
β (deg)	90
γ (deg)	90
$V(\text{\AA}^3)$	4310.8(11)
Ζ	4
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.696
Collected reflections	13621
Unique reflections	2001
R _{int}	0.1881
$2\theta_{\rm max}$	49.988
F_{000}	2240
μ (MoK α)	1.308
Limiting indices	$-31 \le h \le 31$
	$-8 \le k \le 7$
	$-25 \le l \le 25$
Restraints/parameters	307/298
Goodness of fit (F^2)	1.159
$R1 (I > 2\sigma(I))$	0.0878
$wR2 (I > 2\sigma(I))$	0.1296
R1 (all data)	0.1575
wR2 (all data)	0.1576

Table S1. Crystallographic data for L²Ni₂.

¹H NMR titration studies of L^2Ni_2 with M(OTf)_n (NaOTf, KOTf, RbOTf, CsOTf, Ca(OTf)₂, Sr(OTf)₂,Ba(OTf)₂



Fig. S3. ¹H NMR spectral changes of L^2Ni_2 upon the addition of NaOTf (400 MHz, DMSO- d_6 , 0.5 mM).



Fig. S4. ¹H NMR spectral changes of L^2Ni_2 upon the addition of KOTf (400 MHz, DMSO-*d*₆, 0.5 mM).



Fig. S5. ¹H NMR spectral changes of L^2Ni_2 upon the addition of RbOTf (400 MHz, DMSO- d_6 , 0.5 mM).



Fig. S6. ¹H NMR spectral changes of L^2Ni_2 upon the addition of CsOTf (400 MHz, DMSO-*d*₆, 0.5 mM).



Fig. S7. ¹H NMR spectral changes of L²Ni₂ upon the addition of Ca(OTf)₂ (400 MHz, DMSO-*d*₆, 0.5 mM).



Fig. S8. ¹H NMR spectral changes of L^2Ni_2 upon the addition of Sr(OTf)₂ (400 MHz, DMSO- d_6 , 0.5 mM).



Fig. S9. ¹H NMR spectral changes of L^2Ni_2 upon the addition of Ba(OTf)₂ (400 MHz, DMSO- d_6 , 0.5 mM).

ESI-TOF mass spectra of L^2Ni_2 in the presence of $M(OTf)_n$ (NaOTf, KOTf, RbOTf, CsOTf, Sr(OTf)₂, Ba(OTf)₂)



Fig. S10. ESI-TOF mass spectrum of L^2Ni_2 in the presence of NaOTf.



Fig. S11. ESI-TOF mass spectrum of L^2Ni_2 in the presence of KOTf.



Fig. S12. ESI-TOF mass spectrum of L^2Ni_2 in the presence of RbOTf.



Fig. S13. ESI-TOF mass spectrum of L^2Ni_2 in the presence of CsOTf.



Fig. S14. ESI-TOF mass spectrum of L^2Ni_2 in the presence of $Sr(OTf)_2$.



Fig. S15. ESI-TOF mass spectrum of L^2Ni_2 in the presence of Ba(OTf)₂.

UV-Vis titration studies of L²Ni₂ with M(OTf)_n (KOTf, RbOTf, CsOTf, Sr(OTf)₂, Ba(OTf)₂)



Fig. S16. (a) UV-vis spectral changes of L^2Ni_2 upon the addition of KOTf (DMSO, path length 1 cm, 20 μ M), (b) nonlinear curve-fitting of UV absorbance data obtained from the titration study.



Fig. S17. (a) UV-vis spectral changes of L^2Ni_2 upon the addition of RbOTf (DMSO, path length 1 cm, 20 μ M), (b) nonlinear curve-fitting of UV absorbance data obtained from the titration study.



Fig. S18. (a) UV-vis spectral changes of L^2Ni_2 upon the addition of CsOTf (DMSO, path length 1 cm, 20 μ M), (b) nonlinear curve-fitting of UV absorbance data obtained from the titration study.



Fig. S19. (a) UV-vis spectral changes of L^2Ni_2 upon the addition of $Sr(OTf)_2$ (DMSO, path length 1 cm, 20 μ M), (b) nonlinear curve-fitting of UV absorbance data obtained from the titration study.



Fig. S20. (a) UV-vis spectral changes of L^2Ni_2 upon the addition of Ba(OTf)₂ (DMSO, path length 1 cm, 20 μ M), (b) nonlinear curve-fitting of UV absorbance data obtained from the titration study.

¹H NMR titration studies of DB24C8 with M(OTf)_n (NaOTf, KOTf, RbOTf, CsOTf, Sr(OTf)₂, Ba(OTf)₂)



Fig. S21. ¹H NMR spectral changes of DB24C8 upon the addition of NaOTf (400 MHz, DMSO- d_6 , 2.0 mM).



Fig. S22. ¹H NMR spectral changes of DB24C8 upon the addition of KOTf (400 MHz, DMSO-*d*₆, 2.0 mM).



Fig. S23. ¹H NMR spectral changes of DB24C8 upon the addition of RbOTf (400 MHz, DMSO- d_6 , 2.0 mM).



Fig. S24. ¹H NMR spectral changes of DB24C8 upon the addition of CsOTf (400 MHz, DMSO-*d*₆, 2.0 mM).



Fig. S25. ¹H NMR spectral changes of DB24C8 upon the addition of $Sr(OTf)_2$ (400 MHz, DMSO- d_6 , 2.0 mM).



Fig. S26. ¹H NMR spectral changes of DB24C8 upon the addition of Ba(OTf)₂ (400 MHz, DMSO- d_6 , 2.0 mM).

¹H NMR titration studies of H_4L^2 with M(OTf)_n (NaOTf, KOTf, RbOTf, CsOTf, Sr(OTf)₂, Ba(OTf)₂)



Fig. S27. ¹H NMR spectral changes of H_4L^2 upon the addition of NaOTf (400 MHz, DMSO-*d*₆, 0.5 mM).





Fig. S28. ¹H NMR spectral changes of H_4L^2 upon the addition of KOTf (400 MHz, DMSO-*d*₆, 0.5 mM).



Fig. S29. ¹H NMR spectral changes of H_4L^2 upon the addition of RbOTf (400 MHz, DMSO-*d*₆, 0.5 mM).



Fig. S30. ¹H NMR spectral changes of H_4L^2 upon the addition of CsOTf (400 MHz, DMSO-*d*₆, 0.5 mM).



Fig. S31. ¹H NMR spectral changes of H_4L^2 upon the addition of $Sr(OTf)_2$ (400 MHz, DMSO- d_6 , 0.5 mM).



Fig. S32. ¹H NMR spectral changes of H_4L^2 upon the addition of Ba(OTf)₂ (400 MHz, DMSO-*d*₆, 0.5 mM).

DFT calculations of $[L^2Ni^{II}{}_2{}^{\bullet}Cs]^+$ and $[L^2Ni^{I}{}_2{}^{\bullet}Cs]^-$



Fig. S33. DFT optimized structures of (a) $[L^2Ni^{II}_2 \cdot Cs]^+$ and (b) $[L^2Ni^{I}_2 \cdot Cs]^-$ (B3LYP/LANL2DZ).

References

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