Electronic Supplementary Information (ESI)

Homoleptic versus heteroleptic trinuclear systems with mixed L-cysteinate and D-penicillaminate regulated by a diphosphine linker

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1. Tables

Table S1. Luminescence properties of $\mathbf{1_{Zn}}$ and $\mathbf{2_{Zn}}$ in the solid state.

complex	maximum wavelength, λ_{max} / nm	quantum yield, Φ	Lifetime, τ / μs (A_i) [a] and τ_{ave} / μs
$\mathbf{1_{Zn}}$	516	0.04	τ = 0.00488(3468), 0.123(368), 0.761(157) [b] τ_{ave} = 0.532 [b]
$\mathbf{2_{Zn}}$	525	0.05	τ = 0.00472(3879), 0.356 (47), 6.27 (36) [c] τ_{ave} = 5.45 [c]

a: pre-exponential factors; *b*: excited at 405 nm, observed at 520 nm; *c*: *a*: excited at 405 nm, observed at 525 nm.

Table S2. Total energies of the optimized structures

Molecules	Total energy (a.u.)	Total energy (kJ mol^{-1})
[Zn{Au_2(dppm)(L-cys)$_2$}]	-1980.77776390	-5200532.0
[Zn{Au_2(dppm)(D-pen)$_2$}]	-2138.00363347	-5613328.5
[Zn{Au_2(dppm)(L-cys)(D-pen)}]	-2059.38956527	-5406927.3
[Zn{Au_2(dppe)(L-cys)$_2$}]	-2020.08998626	-5303746.3
[Zn{Au_2(dppe)(D-pen)$_2$}]	-2177.31467572	-5716539.7
[Zn{Au_2(dppe)(L-cys)(D-pen)}]	-2098.70289925	-5510144.5

Table S3. Crystallographic data of the compounds.

	$\mathbf{1_{Ni}}$	$\mathbf{2_{Ni}}$	$\mathbf{1_{Zn}}$	$\mathbf{2_{Zn}}$
Formula	$C_{33}H_{48}N_2Au_2NiO_{10}P_2S_2$	$C_{34}H_{52}N_2Au_2NiO_{11}P_2S_2$	$C_{33}H_{48}N_2Au_2ZnO_{10}P_2S_2$	$C_{34}H_{52}N_2Au_2ZnO_{11}P_2S_2$
Colour, form	Green, plate	Blue, plate	Colourless, plate	Colourless, plate
Mw	1211.43	1243.48	1218.09	1250.14
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1$	$P\bar{1}$
a/ Å	18.3452(4)	10.5688(2)	18.4269(4)	10.3527(8)
b/ Å	12.3860(3)	15.8075(3)	12.2826(3)	15.3022(13)
c/ Å	19.8824(4)	16.1811(4)	20.0060(4)	15.8338(13)
α/ °	90	106.128(8)	90	104.376(7)
β/ °	111.973(8)	99.779(7)	111.579(8)	101.422(7)
γ/ °	90	104.476(7)	90	102.993(7)
V/ Å^3	4189.6(3)	2429.84(16)	4210.6(3)	2280.4(3)
Z	4	2	4	2
T/ K	200(2)	200(2)	200(2)	100(2)
F(000)	2352	1212	2360	1216
ρ calcd / g·cm^{-3}	1.921	1.700	1.922	1.821
μ(Mo Kα)/ mm^{-1}	7.660	6.607	7.744	1.615
Crystal size/ mm^3	0.05×0.05×0.02	0.15×0.08×0.01	0.12×0.06×0.01	0.08×0.02×0.02
$R1$ ($I>2\sigma(I)$[a)]	0.0647	0.0785	0.0736	0.1183
w$R2$ (all data)[b)]	0.1220	0.1862	0.1521	0.3162
GOF	1.016	1.003	1.016	0.985

[a] $R_1 = \Sigma(|Fo|-|Fc|)| / \Sigma(|Fo|)$.

[b] $wR_2 = [\Sigma w(Fo^2-Fc^2)^2 / \Sigma w(Fo^2)^2]^{1/2}$.

2. Figures

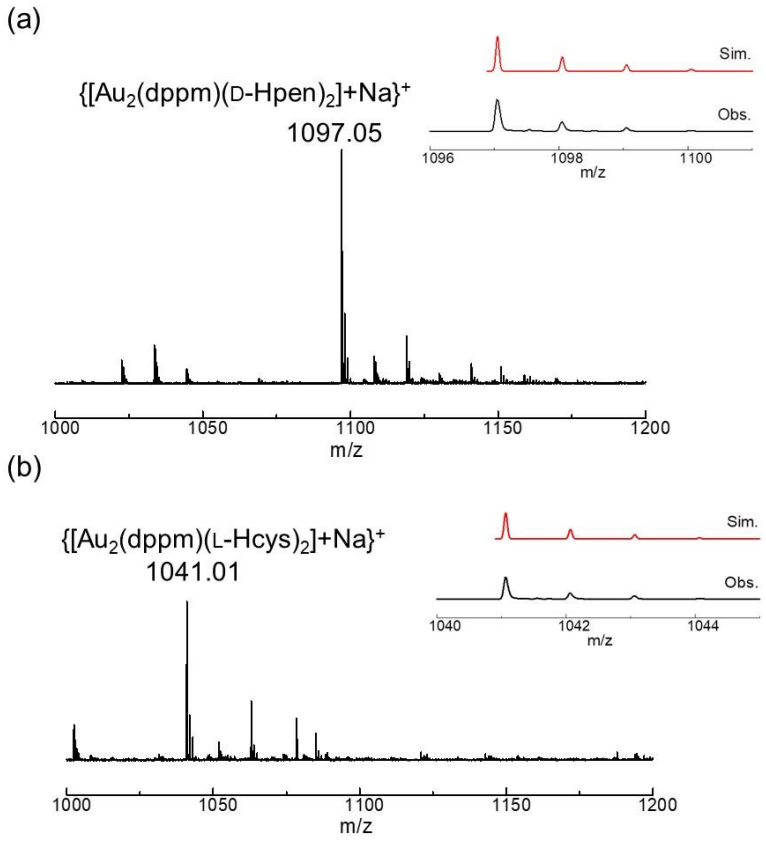

Fig. S1. ESI-TOF mass spectra (positive mode) of the *in situ*-prepared metalloligands, (a) $[Au_2(dppm)(D\text{-}pen)_2]^{2-}$ ($L1^{dppm}$) and (b) $[Au_2(dppm)(L\text{-}cys)_2]^{2-}$ ($L2^{dppm}$) in methanol-water (1:1). Inset: the isotope patterns of the dominant signals at *m*/*z* = 1097 and 1041 with the simulated patterns.

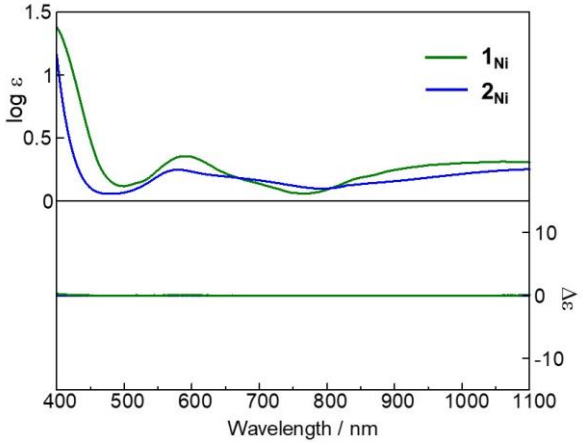

Fig. S2. Absorption spectra of $\mathbf{1_{Ni}}$ and $\mathbf{2_{Ni}}$ in methanol-water (1:1).

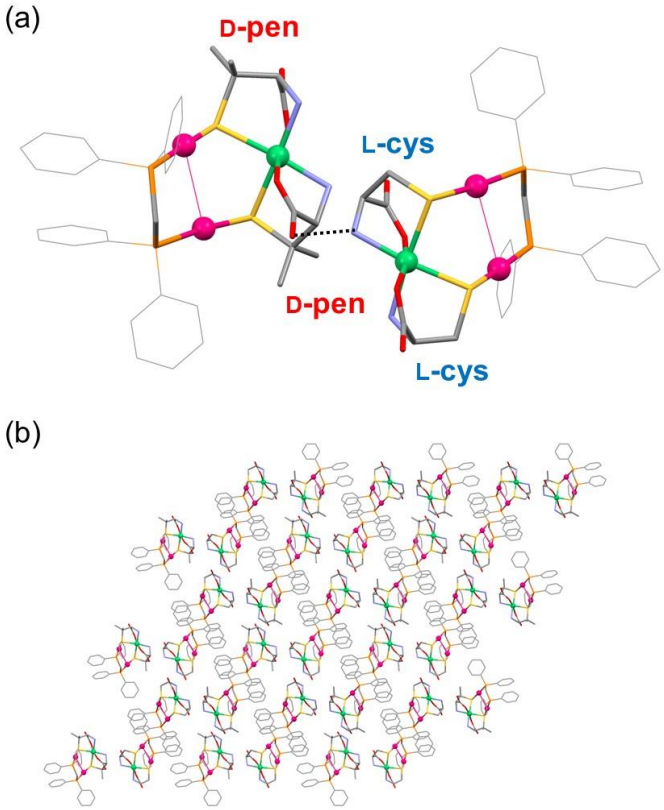

Fig. S3. Perspective views of (a) [Ni(L1^{dppm})] and [Ni(L2^{dppm})] molecules with an intermolecular NH···O hydrogen bond (dashed line) and (b) a packing structure viewed from the crystallographic *b*-axis of $\mathbf{1}_{Ni}$. Colour code: Au, pink; Ni, blue-green; S, yellow; P, orange; O, red; N, blue; and C, grey. H atoms were omitted for clarity.

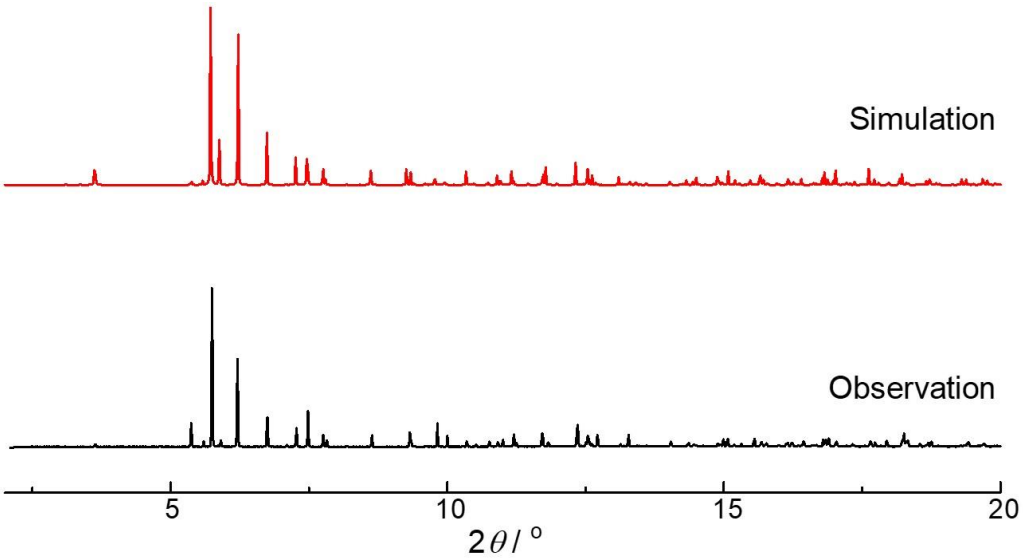

Fig. S4. Simulated (red) and observed (black) powder X-ray diffraction patterns of $\mathbf{1}_{Ni}$.

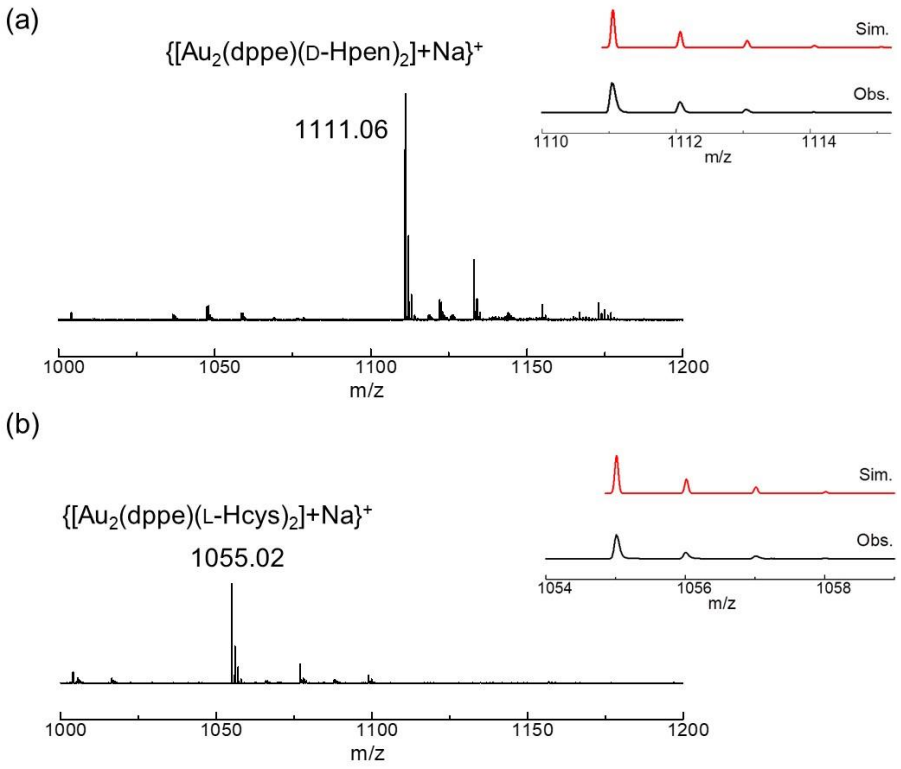

Fig. S5. ESI-TOF mass spectra (positive mode) of the *in situ*-prepared metalloligands, (a) $[Au_2(dppe)(D\text{-}pen)_2]^{2-}$ ($L1^{dppe}$) and (b) $[Au_2(dppe)(L\text{-}cys)_2]^{2-}$ ($L2^{dppe}$) in methanol-water (1:1). Inset: the isotope patterns of the dominant signals at *m*/*z* = 1111 and 1055 with the simulated patterns.

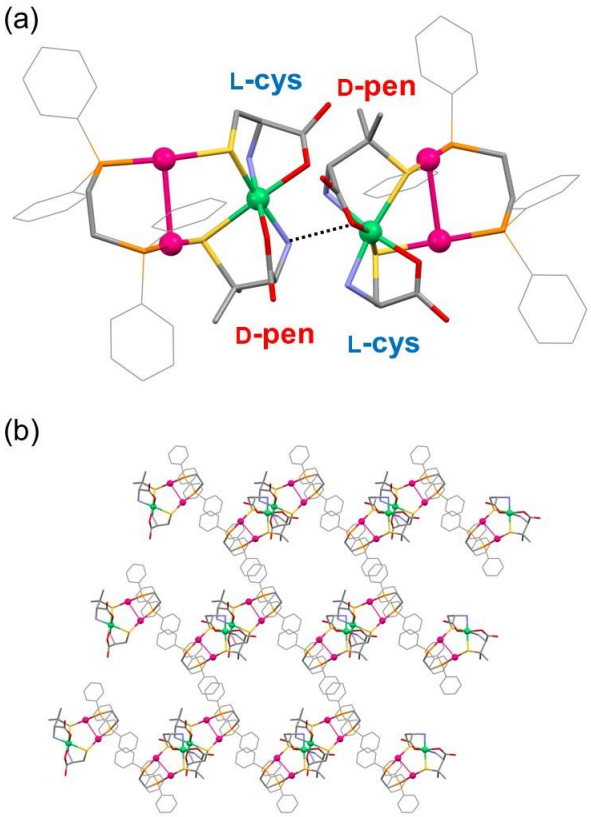

Fig. S6. Perspective views of (a) *C*-[Ni(L3^{dppe})] and *A*-[Ni(L3^{dppe})] molecules with an intermolecular NH···O hydrogen bond (dashed line) and (b) a packing structure viewed from crystallographic *a*-axis of **2**$_{Ni}$. Colour code: Au, pink; Ni, blue-green; S, yellow; P, orange; O, red; N, blue; and C, grey. H atoms were omitted for clarity.

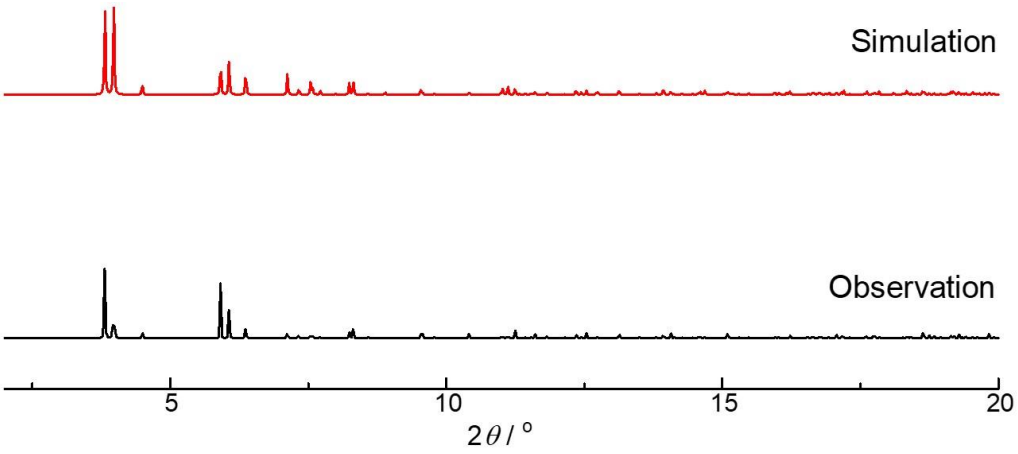

Fig. S7. Simulated (red) and observed (black) powder X-ray diffraction patterns of **2**$_{Ni}$.

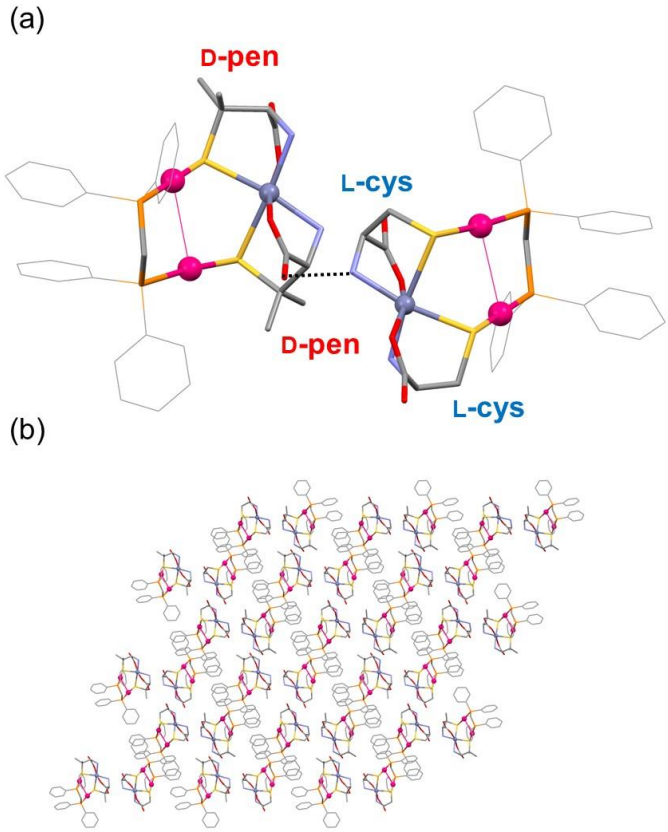

Fig. S8. Perspective views of (a) [Zn(L1^{dppm})] and [Zn(L2^{dppm})] molecules with an intermolecular NH···O hydrogen bond (dashed line) and (b) a packing structure viewed from the crystallographic *b*-axis of **1**$_{Zn}$. Colour code: Au, pink; Zn, pale-purple; S, yellow; P, orange; O, red; N, blue; and C, grey. H atoms were omitted for clarity.

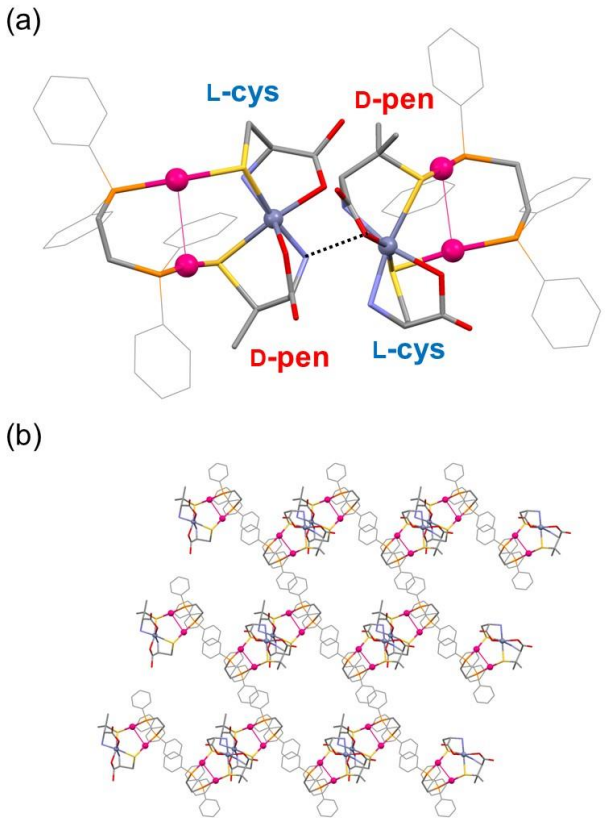

Fig. S9. Perspective views of (a) *C*-[Zn(L3^{dppe})] and *A*-[Zn(L3^{dppe})] molecules with an intermolecular NH···O hydrogen bond (dashed line) and (b) a packing structure viewed from crystallographic *a*-axis of $\mathbf{2}_{\mathbf{Zn}}$. Colour code: Au, pink; Zn, pale-purple; S, yellow; P, orange; O, red; N, blue; and C, grey. H atoms were omitted for clarity.

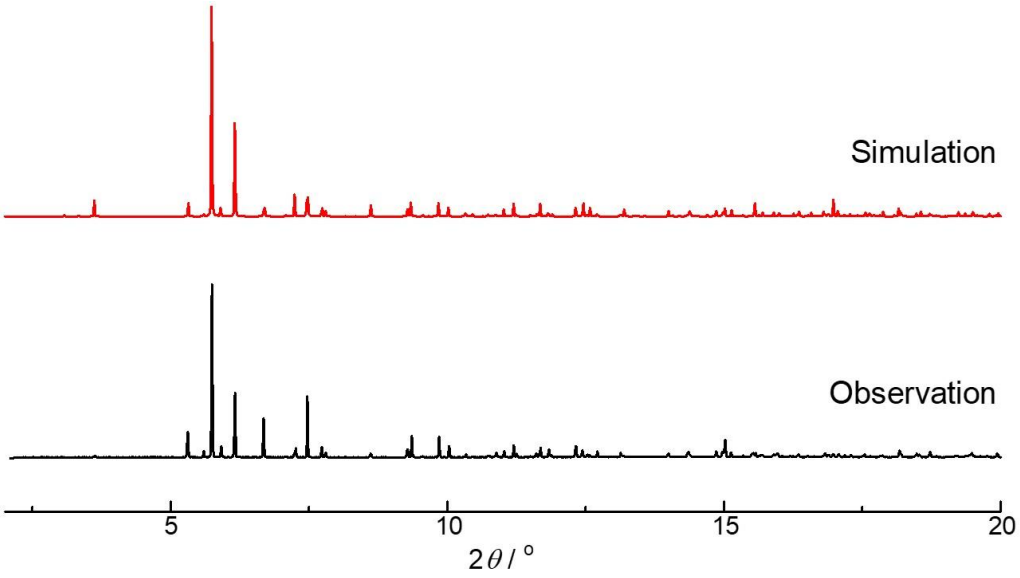

Fig. S10. Simulated (red) and observed (black) powder X-ray diffraction patterns of $\mathbf{1}_{\mathbf{Zn}}$.

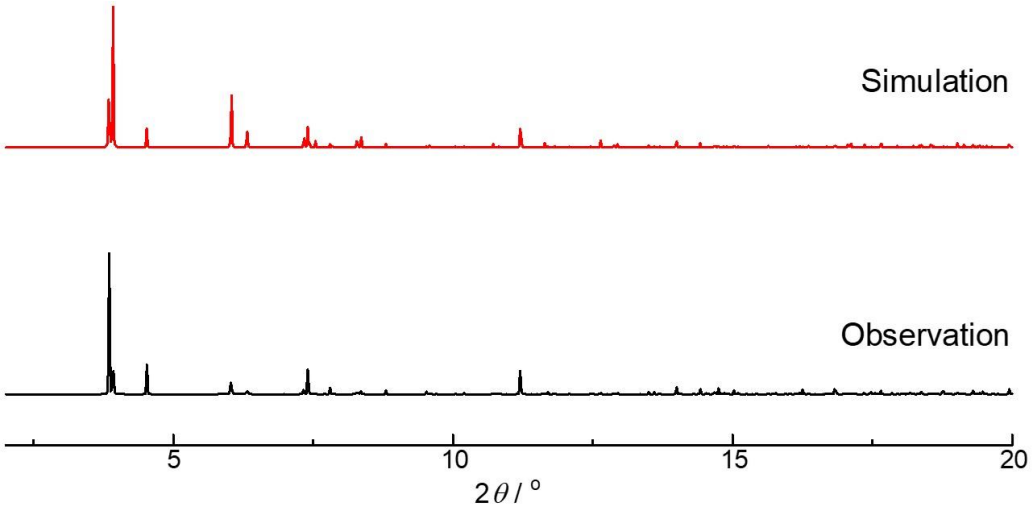

Fig. S11. Simulated (red) and observed (black) powder X-ray diffraction patterns of $\mathbf{2_{Zn}}$.

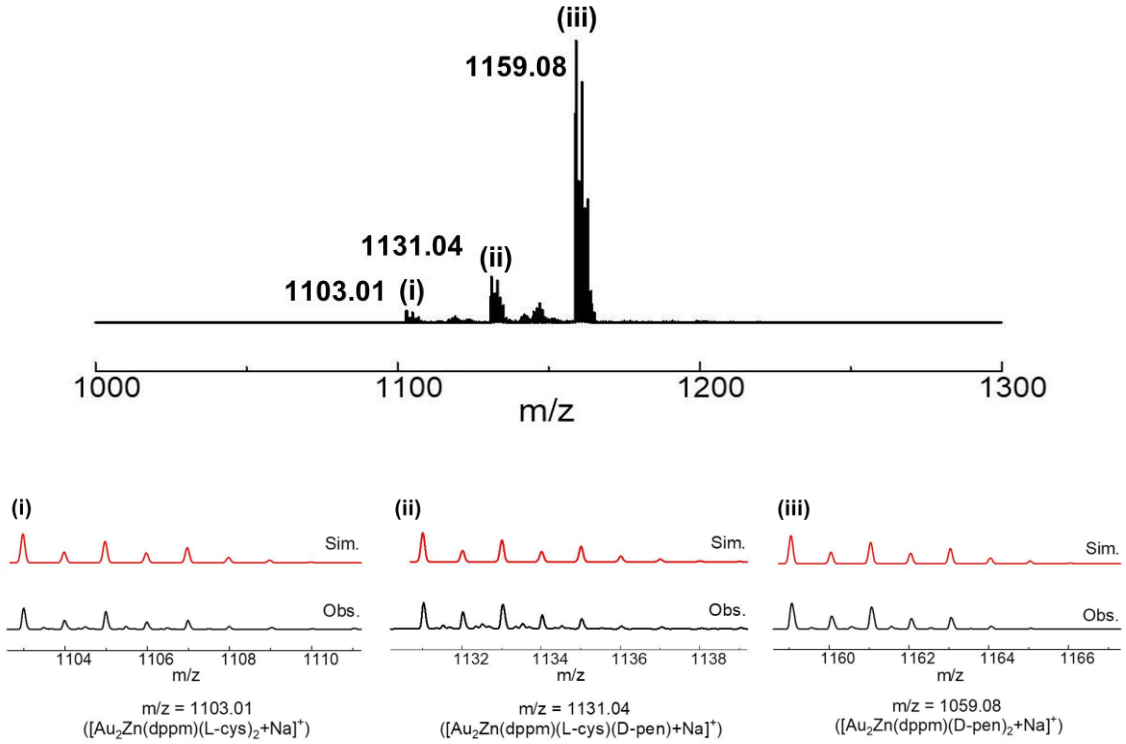

Fig. S12. ESI mass spectra of the reaction mixture of $L1^{dppm}$, $L2^{dppm}$ and zinc acetate in methanol-water (1:1): (i) $[Zn\{Au_2(dppm)(L\text{-}cys)_2\}+Na]^+$ (m/z = 1103.01), (ii) $[Zn\{Au_2(dppm)(L\text{-}cys)(D\text{-}pen)\}+Na]^+$ (m/z = 1131.04) and (iii) $[Zn\{Au_2(dppm)(D\text{-}pen)_2\}+Na]^+$ (m/z = 1159.08).

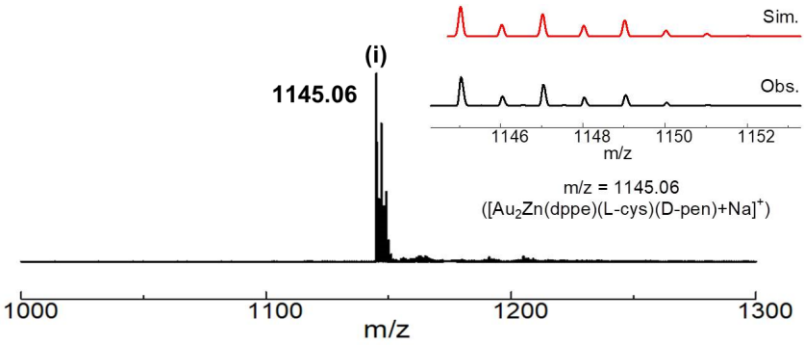

Fig. S13. ESI mass spectra of the reaction mixture of $L1^{dppe}$, $L2^{dppe}$ and zinc acetate in methanol-water (1:1): (i) $[Zn\{Au_2(dppe)(L\text{-}cys)(D\text{-}pen)\}+Na]^+$ (m/z = 1145.06).