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Aggregation behavior of group 12 complexes of a tripodal mixed NS(thiolato) donor ligand

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ELECTRONIC SUPPLEMENTARY INFORMATION

Additional Experimental Details

Crystallization of additional solvates of 1. One equivalent of $CdCl_2$ (50 mM in MeOH, 10 mL, 50 mmol) was added dropwise to a stirred solution containing 2.5 mL MeOH, NaOH (0.2 M in MeOH, 2.5 mL, 50 mmol) and **LH** (0.1 M in MeOH, 5.0 mL, 50 mmol). Transient cloudiness occurred during the addition. The solution was divided into 1 mL aliquots. Various cosolvents (0.2, 0.5 and 1.0 mL) were mixed with each aliquot before setting aside for slow evaporation. After three weeks, diffraction quality crystals were obtained in low yield of **1**·m-xylene with m-xylene as cosolvent and of **1**·MeOH with ethyl acetate as the cosolvent. Both crystals became opaque when vacuum dried.

Single Crystal Diffraction of additional solvates of 1. Single crystal diffraction data for additional solvates were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å) on a Bruker D8 Venture Photon 3. The structures were solved by intrinsic phasing and refined on F^2 by full-matrix least squares using the ShelXle 2019/3 program package.[1] All non-hydrogen atoms were refined anisotropically and the hydrogens were placed theoretically. Crystallographic data for **1**·m-xylene and **1**·MeOH are provided in Table S1. Selected bond distances and angles are provided in Table S2.

Brief overview of the structures of additional solvates of 1

The neutral dinuclear complex $[Cd\mathbf{L}Cl]_2$·m-xylene (**1**·m-xylene) crystallized in the triclinic space group *P*-1 with one dimeric complex and one disordered m-xylene molecule per unit cell. Both the complex and the m-xylene molecule lie on crystallographic inversion centers. Although not isomorphic, bond distances and bond angles for **1**·are comparable in the m-xylene (Table S2) and·benzene (Table 4) solvates. The distorted envelope ring conformations have matching flap positions.

The neutral dinuclear complex $[Cd\mathbf{L}Cl]_2$·MeOH (**1**·MeOH) crystallized in the monoclinic space group *C*2/*c* with one dimeric complex and one disordered methanol molecule per unit cell. The complex lies on a crystallographic inversion center and the methanol lies on a C_2 axis. Bond distances and bond angles for **1**·MeOH (Table S2) are comparable to the other two solvates of **1**. The distorted envelope ring conformations also have matching flap positions.

Table S1. Crystallographic data for additional [Cd**L**Cl]$_2$ solvates.

Solvate	m-xylene	MeOH
Empirical Formula	$C_{36}H_{42}Cd_2Cl_2N_6S_2$	$C_{29}H_{36}Cd_2Cl_2N_6OS_2$
Formula mass [g mol^{-1}]	918.57	844.46
Crystal Size [mm^3]	0.147 × 0.144 × 0.131	0.191 × 0.140 × 0.063
Crystal System	Triclinic	Monoclinic
Space Group	*P*-1	*C*2/*c*
a[Å]	9.5643(6)	21.3846(7)
b[Å]	9.6576(6)	9.4379(3)
c[Å]	11.1260(7)	16.6623(5)
α[°]	104.832(2)	90
β[°]	105.857(2)	101.6100(10)
γ[°]	91.085(2)	90
V[Å^3]	951.27(10)	3294.08(18)
Z	1	4
Radiation (monochromatic)	Mo Kα	Mo Kα
T [K]	133(2)	100(2)
ρ_{calc} [Mg m^{-3}]	1.603	1.703
λ [Å]	0.71073	0.71073
μ [mm^{-1}]	1.402	1.613
Measured reflections	55715	42613
Ind. Reflections [$R_{(int)}$]	3739 [0.0399]	3252 [0.0510]
Completeness to θ = 25.242°	99.3%	100.0%
Data/restraints/parameters	3739 / 0 / 255	3252 / 177 / 200
R1[a], wR2[b] [$I > 2\sigma(I)$]	0.0140, 0.0363	0.0280, 0.0647
R1[a], wR2[b] (all data)	0.0144, 0.0365	0.0309, 0.0662
Goodness-of-fit (GOF)	1.053	1.128

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

Table S2. Selected bond lengths and angles for additional [Cd**L**Cl]$_2$ solvates.

Solvate	m-xylene	methanol
M–N1A	2.4137(11)	2.396(3)
M–N1B	2.4519(12)	2.417(2)
M–N	2.4742(11)	2.493(3)
M–S	2.6343(4)	2.6309(8)
M–Cl	2.5010(3)	2.5327(8)
M–S#1	2.6627(4)	2.6490(8)
N1A–M–N1B	87.63(4)	91.43(8)
N1A–M–N	69.41(4)	68.20(9)
N1B–M–N	70.61(4)	71.09(8)
N1A–M–Cl	96.98(3)	95.42(7)
N1B–M–Cl	91.25(3)	90.16(7)
N–M–Cl	157.22(3)	154.09(6)
N1A–M–S	149.01(3)	148.13(7)
N1B–M–S	85.87(3)	83.80(6)
N–M–S	79.86(3)	80.51(6)
Cl–M–S	113.412(12)	116.03(3)
N1B–M–S#1	165.44(3)	165.66(7)
N1A–M–S#1	90.21(3)	86.21(6)
N–M–S#1	95.16(3)	94.96(6)
Cl–M–S#1	103.306(12)	104.13(3)
S–M–S#1	88.608(11)	90.75(2)
M–S–M#1	91.393(11)	89.26(2)

m-xylene solvate symmetry code: #1: –x + 2, –y + 1, –z + 1; methanol solvate symmetry code: #1: –x + 3/2, –y + 1/2, –z + 1

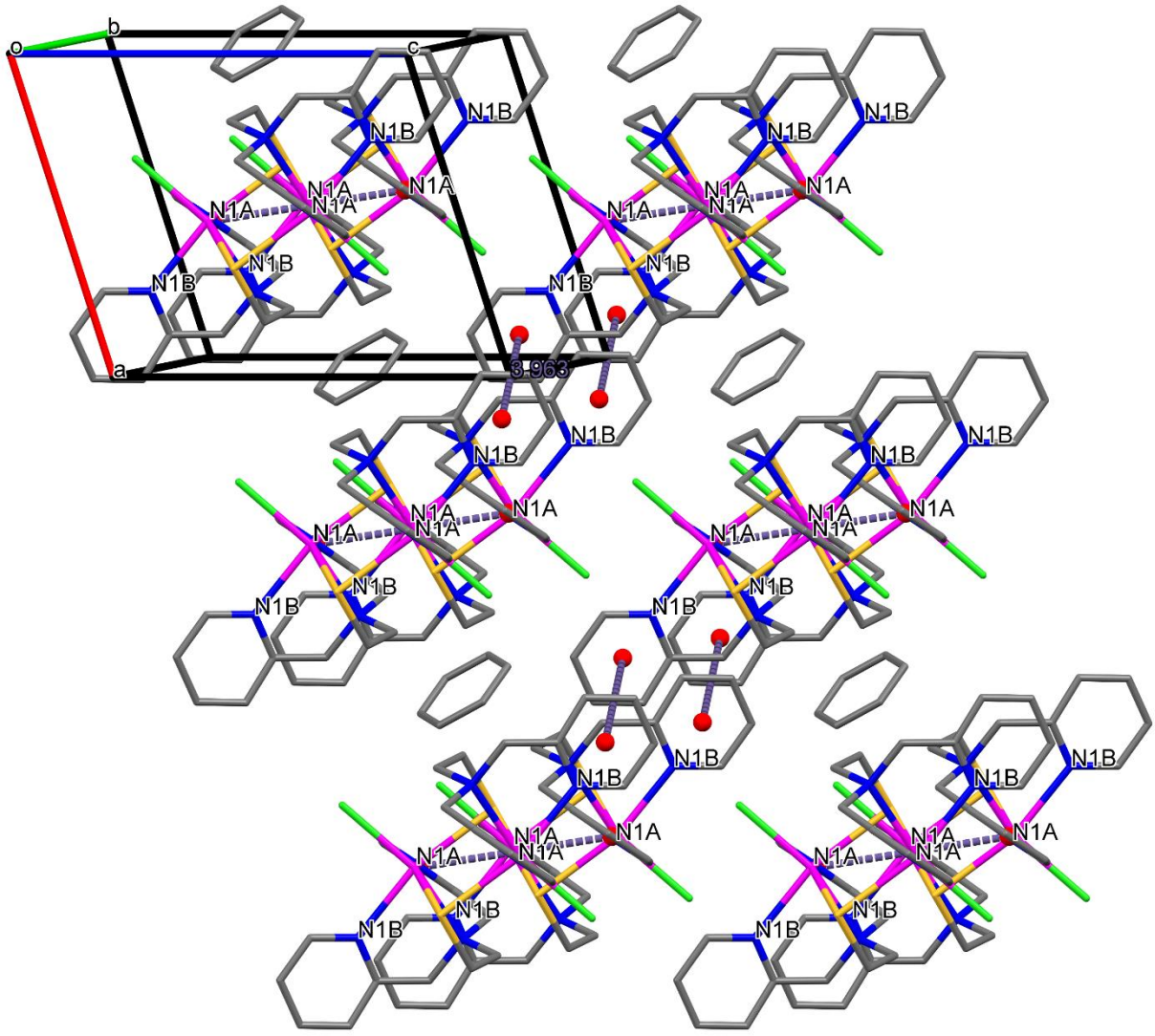


Figure S1. Stacking diagram of **1** along *b** showing formation of sheets through pairwise N1A pyridyl (5.198 Å centroid–centroid separation; 3.526 Å normal separation) and N1B pyridyl (3.963 Å centroid–centroid separation; 3.297 Å normal separation) offset face-to-face interactions[2] or C–H π attractions.[3] Benzene molecules are located between sheets and potentially involved in a weak multimolecular embrace with four neighboring N1A pyridyl rings.[4] Hydrogen atoms omitted for clarity.

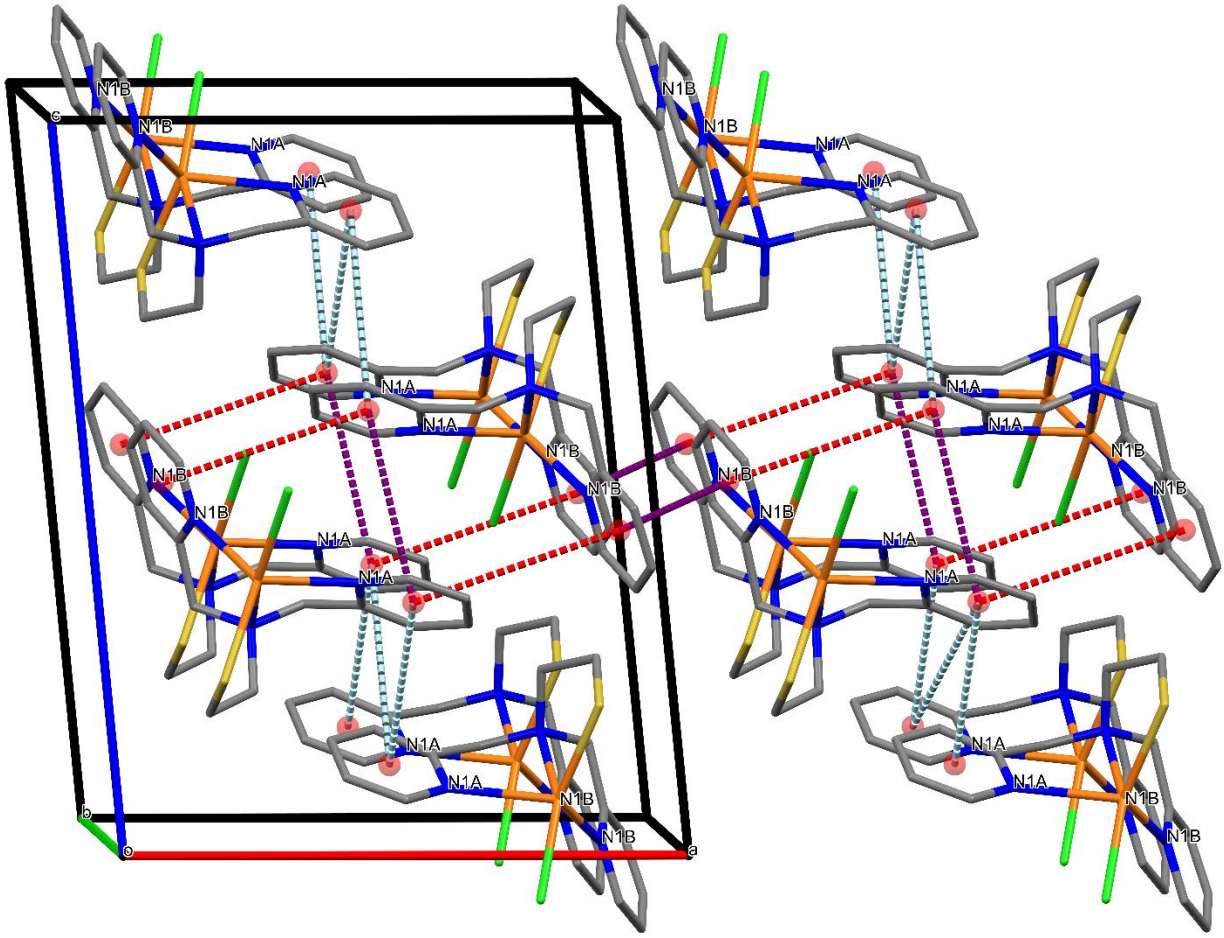


Figure S2. Stacking diagram of **2** along *b* showing formation of strands along the *a* direction through pairwise N1B (3.598 Å centroid–centroid separation; 3.349 Å normal separation) and N1A (4.385 Å centroid–centroid separation; 3.884 Å normal separation) pyridyl ring OFF interactions as well as EF interactions between N1A and N1B pyridyl rings (4.811 Å centroid–centroid separation; 4.391 Å normal separation).[2, 5] The chains are networked with their neighbors through a zig-zag aryl embrace between N1A pyridyl rings (5.554 Å centroid–centroid separation; 5.183 Å normal separation).[4] Hydrogen atoms omitted for clarity. OFF in violet; EF in red; aryl embrace EF interactions in light blue.

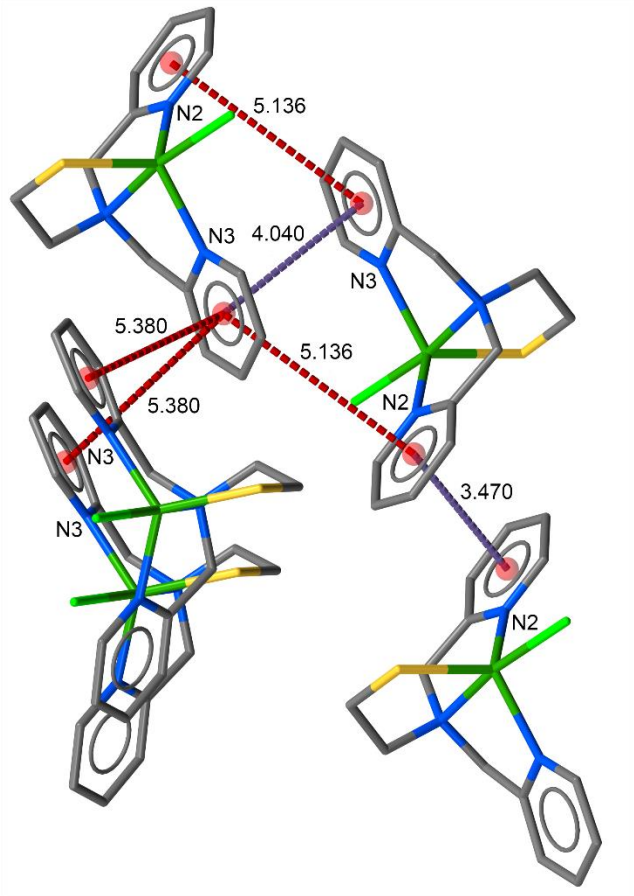


Figure S3. Intermolecular aromatic distances (Å) between pyridyl rings, identified by their nitrogen atoms, in **3** (CDC Refcode XALTEJ) [6]. Hydrogen atoms are omitted for clarity. OFF in violet; EF in red.

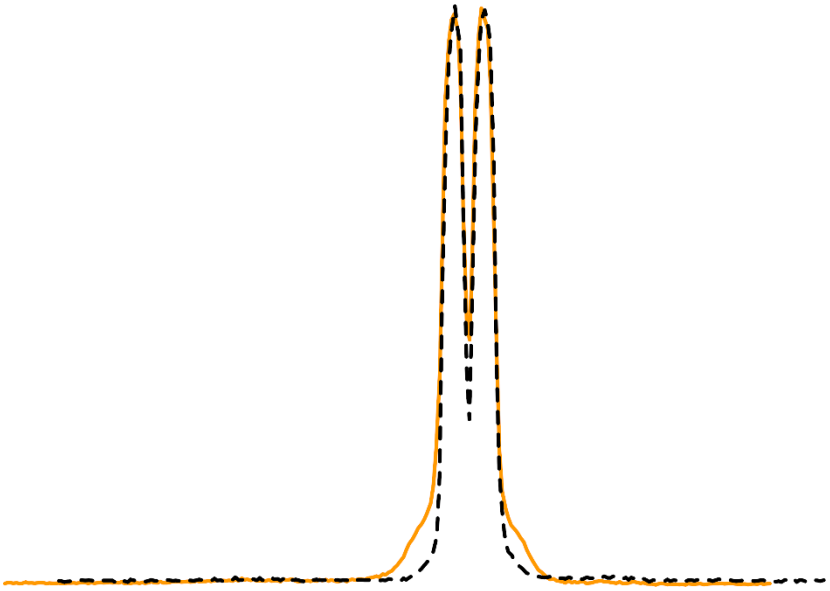


Figure S4. Overlay of H_a resonances for **2** (CD_3CN; nominally 5 mM) at 60 °C (dashed black) and –40 °C (solid orange) accentuating the partially resolved $J(^{199}Hg^{1}H)$ coupling satellites.

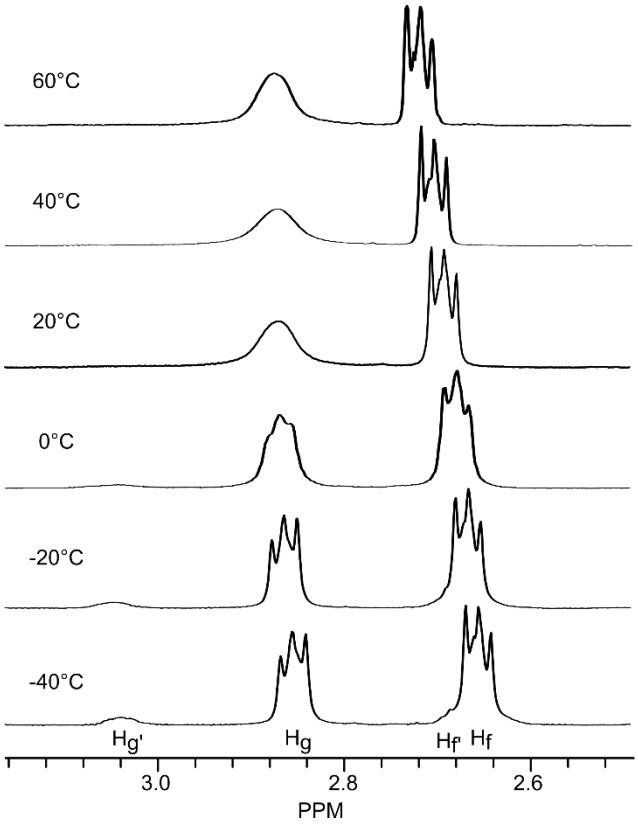


Figure S5. Ethylene proton NMR highlights of **2** (CD_3CN, nominally 5 mM) as a function of temperature. Resonances assigned to a minor environment in slow exchange on the chemical shift time scale at low temperature are labeled with primes.

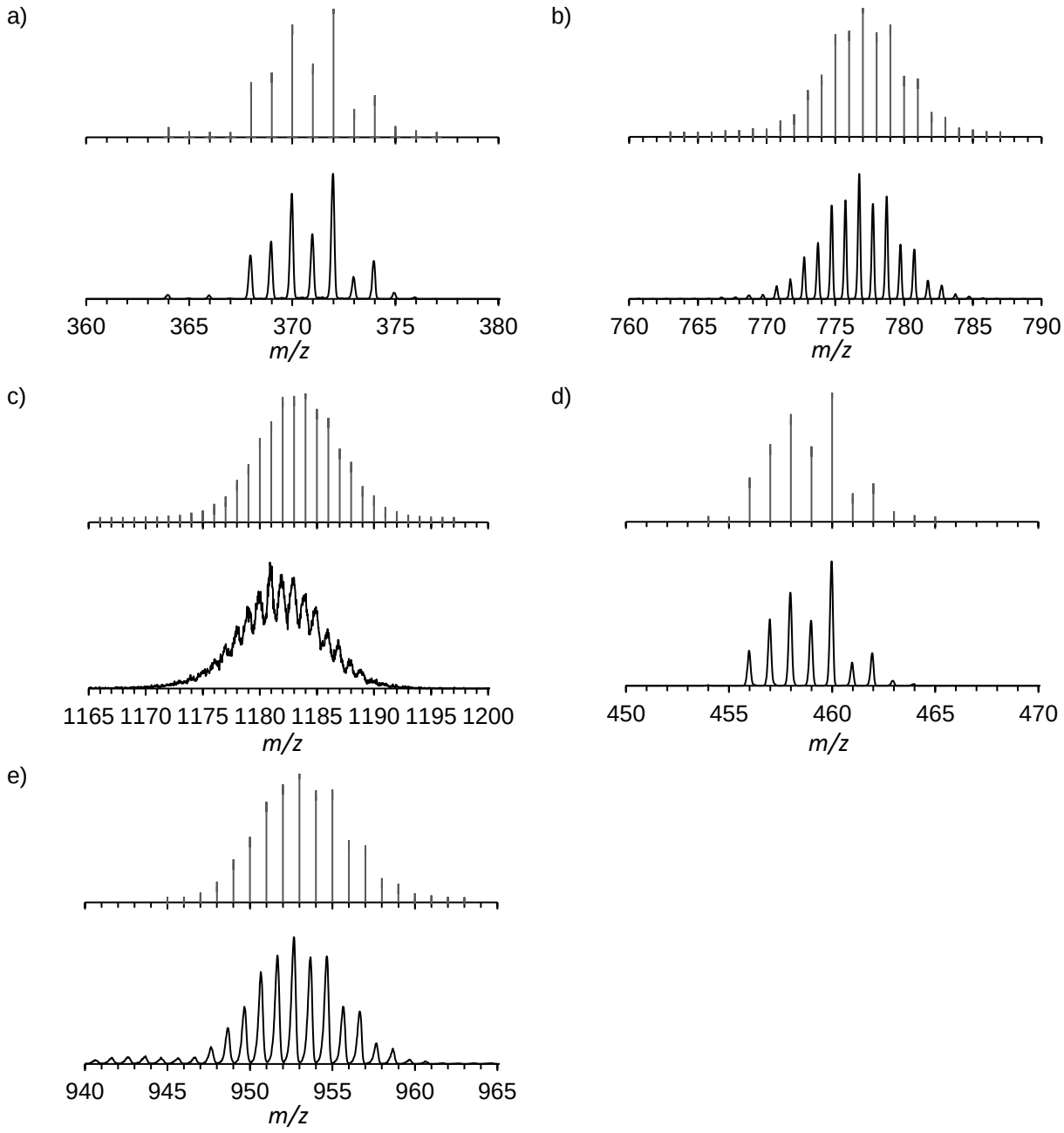
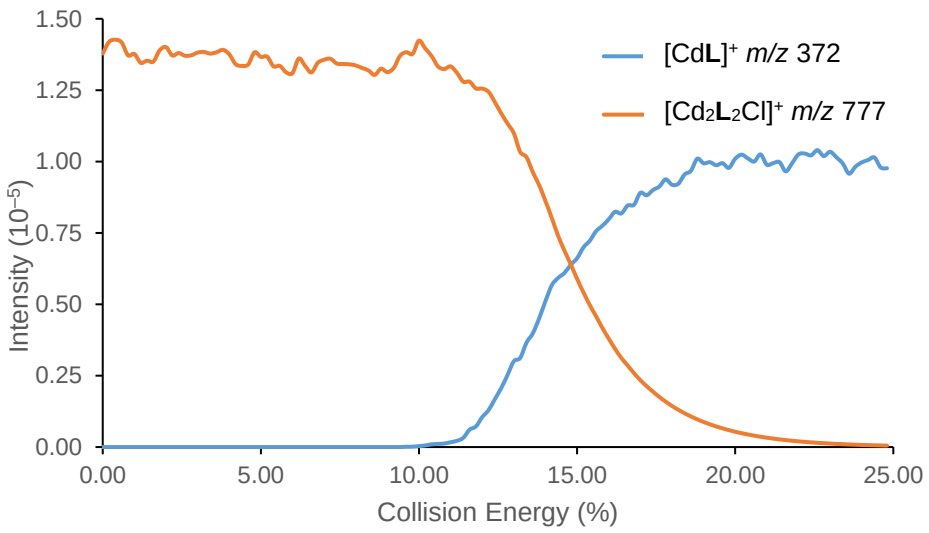


Figure S6. Calculated isotope pattern (top) and observed positive ion direct infusion ESI-MS ZoomScan isotope pattern (bottom) of (a) $[Cd\mathbf{L}]^+$, (b) $[Cd_2\mathbf{L}_2Cl]^+$, (c) $[Cd_3\mathbf{L}_3Cl_2]^+$, (d) $[Hg\mathbf{L}]^+$ and (e) $[Hg_2\mathbf{L}_2Cl]^+$.

a)



b)

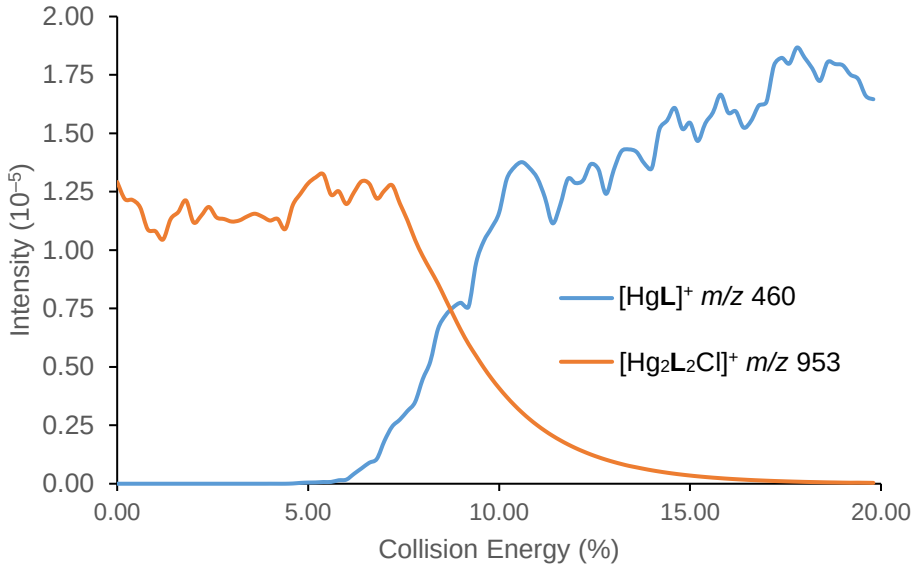


Figure S67 Collision energy plots following the intensity of the most abundant isotopomers for a) [Cd**L**]$^+$ and [Cd$_2$**L**$_2$Cl]$^+$ and b) [Hg**L**]$^+$ and [Hg$_2$**L**$_2$Cl]$^+$.

References

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