Electronic Supplementary Material (ESI) for ChemComm.

Postsynthetic Modification of Cadmium-Based Molecular Links and Knots

Thirumurugan Prakasam,[a] Rana A. Bilbeisi,[a] Matteo Lusi,[b] John-Carl Olsen,[c] Carlos Platas-Iglesias,[d] and Ali Trabolsi[1*]

[a]*New York University Abu Dhabi (NYUAD), Experimental Research Building C-1, Saadiyat Island, Abu Dhabi, UAE.*

[b]*Department of Chemical and Environmental Science, University of Limerick, Limerick, Republic of Ireland.*

[c]*School of Sciences, Indiana University Kokomo, Kokomo, IN 46904, USA.*

[d]*Departamento de Química Fundamental, Universidade de Coruña, Campus da Zapateira, Rúa da Farga 10, 15008 A Coruña, Spain.*

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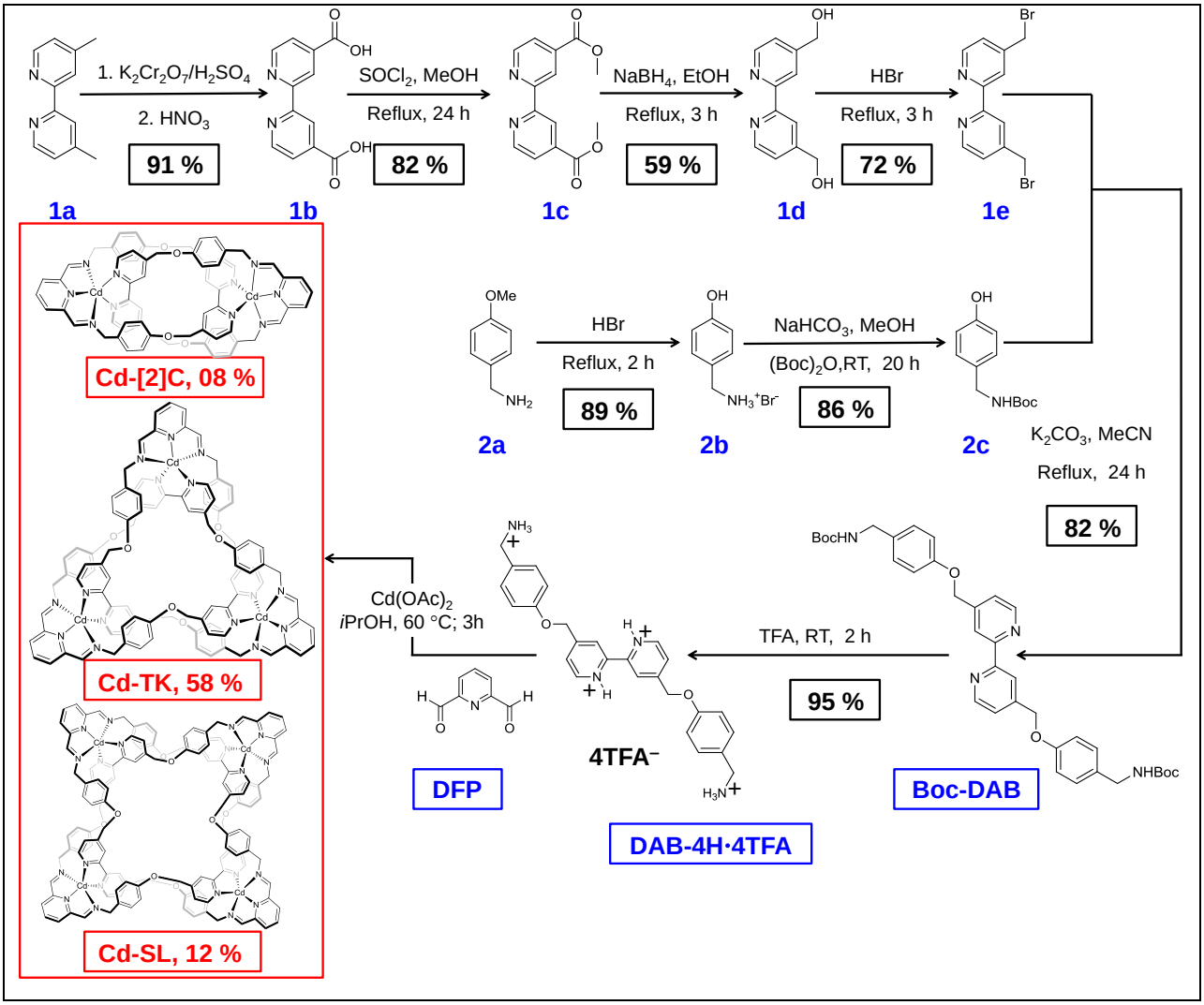
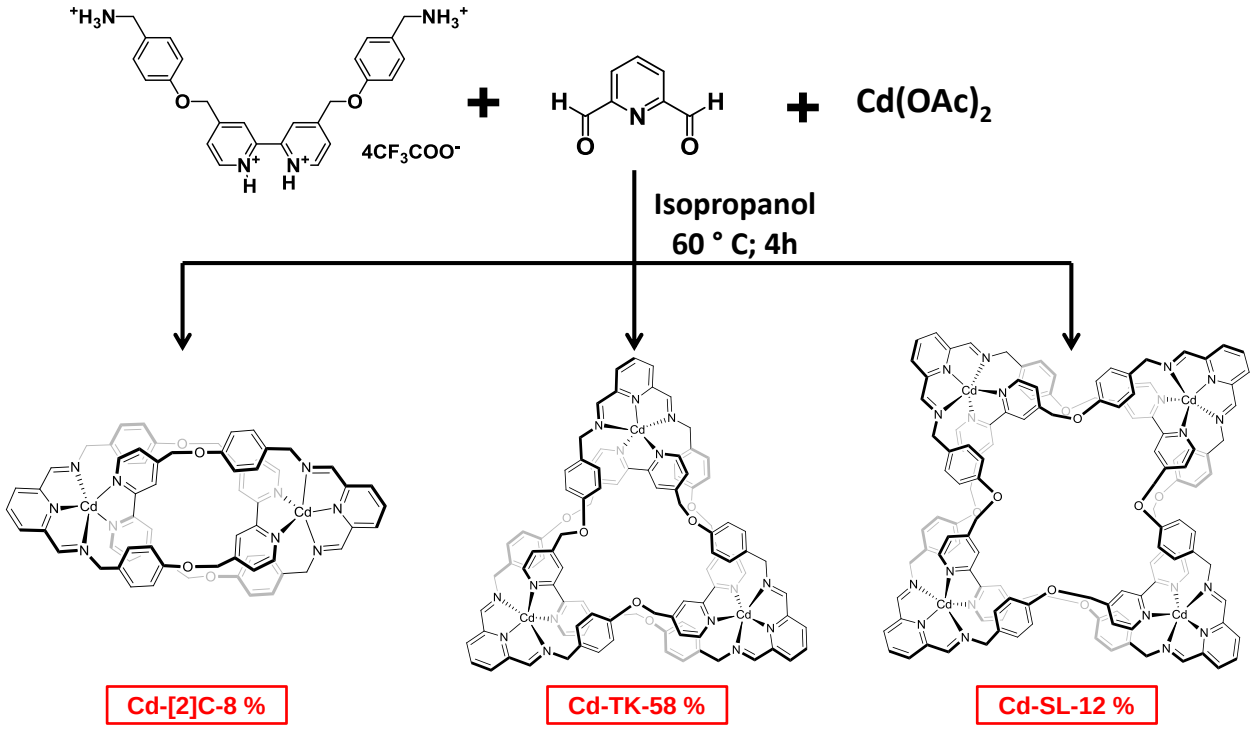
1. General materials and methods

All reagents and starting materials were purchased from Sigma-Aldrich and used without further purification. The diamino bipyridine (DAB) ligand and 2,6-diformyl pyridine were synthesized as previously reported.[1] Thin-layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). The plates were inspected with UV light. Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Routine nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance III spectrometer, with working frequencies of 600 and 500 MHz for ^{1}H, and 151.0 and 125.0 MHz for ^{13}C nuclei. All chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CD_3CN: δ = 1.94 ppm, CD_3OD: δ = 3.31 ppm).[2] All ^{13}C spectra were recorded with the simultaneous decoupling of proton nuclei. Coupling constant values (*J*) are given in hertz (Hz). The multiplicity of the proton spectrum is abbreviated in the following way: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), qt (quintet), sx (sextet), m (multiplet) and a wide signal is preceded by br (broad). High resolution mass spectrometry (HRMS) analyses were performed using an Agilent 6540 UHA Accurate Mass Q-TOF / LC - MS-spectrometer in the positive mode and an acetonitrile/water used a gradient in C-18 column.

2. Synthetic strategy for the preparation of the dynamic library of cadmium based molecular links



3. Synthesis of the dynamic library of cadmium based molecular links



DAB-4H·4TFA was prepared according to a previous synthetic report with slight modifications. Freshly prepared **DAB-4H·4TFA** (0.264 g, 0.3 mmol) was added to 2,6-diformyl pyridine (0.040 g, 0.3 mmol) and cadmium acetate (0.067 g, 0.3 mmol) in isopropanol. The reaction mixture was stirred at 60 °C for 3 h. After 1 h, a pale yellow solid started to precipitate from the reaction mixture. After completion of the reaction, the pale yellow precipitate was filtered and dried under vacuum for 4 h to give Cd-TK. The filtrate was kept at room temperature for 3-4 days. After 4 days, a light yellow solid precipitated from the mother liquor and was collected by filtration and dried under vacuum to yield Cd-SL. The remaining mother liquor was concentrated to dryness to give Cd-[2]C. Characterization details for the three molecular links are given below.

Cd-[2]C: 20.8 mg, 8%; ^{1}H NMR (500 MHz, MeOH-d4, 25 °C): δ 4.81 (s, 8H, Ar-CH_2), 5.09 (s, 8H, Ar-CH_2), 6.18 (d, 8H, *J* = 8.8 Hz, Ar-*H*),), 6.53 (brs, 8H, Ar-*H*), 7.61 (brs, 4H, Ar-*H*), 8.02 (brs, 4H, Ar-*H*), 8.27 (s, 4H, Ar-*H*), 8.29 (d, 4H, *J* = 7.8 Hz, Ar-*H*), 8.61 (t, 2H, *J* = 7.8 Hz, Ar-*H*), 8.88 (s, 4H, Ar-*H*); ^{13}C NMR (125 MHz, MeOH-d4, 25 °C): δ 62.6, 66.4, 114.0, 118.6 (q, $^{2}J_{C\text{-}F}$ = 263 Hz, TFA), 120.6, 124.7, 128.9, 129.3, 129.9, 137.8, 143.2, 148.1, 148.5, 150.4,

156.7, 158.5, 161.2 (q, $^{3}J_{C\text{-}F}$ = 33 Hz. TFA); MS (ESI-MS): m/z Calcd for $(C_{70}H_{54}Cd_2F_6N_{10}O_8)^{2+}$: 751.0965 $[M-2TFA]^{2+}$, found: 751.1067 $[M-2TFA]^{2+}$.

Cd-TK: 150.87 mg, 58%; ^{1}H NMR (500 MHz, MeOH-d4, 25 °C): δ 4.80 (brs, 12H, Ar-C*H*$_2$), 5.11 (ABq, 12H, *J* = 8.4 Hz, Ar-C*H*$_2$), 6.45 (d, 12H, *J* = 8.4 Hz, Ar-*H*), 6.48 (d, 12H, *J* = 8.4 Hz, Ar-*H*), 7.65 (d, 6H, *J* = 5.1 Hz, Ar-*H*), 8.12 (d, 6H, *J* = 5.1 Hz, Ar-*H*), 8.32 (d, 6H, *J* = 7.9 Hz, Ar-*H*), 8.61 (t, 3H, *J* = 7.8 Hz, Ar-*H*), 8.99 (s, 6H, Ar-*H*), 9.19 (brs, 6H, Ar-*H*); ^{13}C NMR (125 MHz, MeOD-d4, 25 °C): δ 61.5, 68.2, 114.2, 115.1, 123.5 (q, $^{2}J_{C\text{-}F}$ = 266 Hz, TFA), 128.4, 129.4, 130.0, 130.4, 143.5, 147.4, 148.2, 149.2, 150.8, 158.0, 160.2, 162.0 (q, $^{3}J_{C\text{-}F}$ = 32 Hz. TFA); MS (ESI-MS): m/z Calcd for $(C_{107}H_{78}Cd_3F_{12}N_{15}O_{14})^{2+}$: 1183.1376 $(M—2TFA)^{2+}$, found: 1183.1489 $[M—2TFA]^{2+}$; m/z Calcd for $(C_{105}H_{78}Cd_3F_9N_{15}O_{12})^{3+}$: 751.0965 $[M—3CTFA]^{3+}$, found: 751.1049 $[M—3TFA]^{3+}$.

Cd-SL: 31.2 mg, 12%; ^{1}H NMR (500 MHz, MeOH-d4, 25 °C): δ 4.65 (ABq, 16H, *J* = 15.7 Hz, Ar-C*H*$_2$), 5.03 (ABq, 16H, *J* = 12.9 Hz, Ar-C*H*$_2$), 6.47 (ABq, 32H, *J* = 7.8 Hz, Ar-*H*), 7.80 (d, 8H, *J* = 4.4 Hz, Ar-*H*), 8.28 (d, 16H, *J* = 7.8 Hz, Ar-*H*), 8.53 (brs, 8H, Ar-*H*), 8.58 (t, 4H, *J* = 7.8 Hz, Ar-*H*), 8.96 (brs, 8H, Ar-*H*); ^{13}C NMR (125 MHz, MeOD-d4, 25 °C): δ 60.6, 67.5, 114.2, 119.0 (q, $^{2}J_{C\text{-}F}$ = 268 Hz, TFA), 120.9, 124.7, 129.1, 129.3, 129.9, 143.4, 147.4, 148.2, 148.9, 150.5, 157.0, 160.5, 163.4 (q, $^{3}J_{C\text{-}F}$ = 32 Hz. TFA); MS (ESI-MS): m/z Calcd for $(C_{144}H_{104}Cd_4F_{18}N_{20}O_{20})^{2+}$: 1615.1786 $[M—2TFA]^{2+}$, found: 1615.1993 $[M—2TFA]^{2+}$, m/z Calcd for $(C_{142}H_{104}Cd_4F_{15}N_{20}O_{18})^{3+}$: 1039.1239 $[M—3TFA]^{3+}$, found: 1039.1381 $[M—3TFA]^{3+}$.

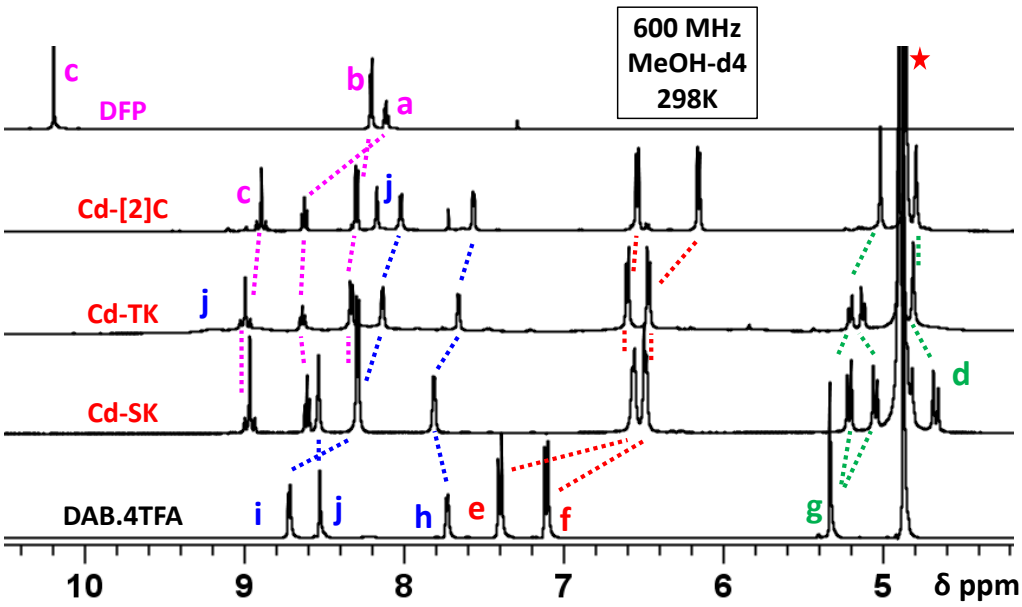


Figure S1. Partial ^{1}H NMR spectra of Cd-[2]C, Cd-TK, and Cd-SL aligned with spectra of DFP and DAB in MeOD-d4 at 298 K.

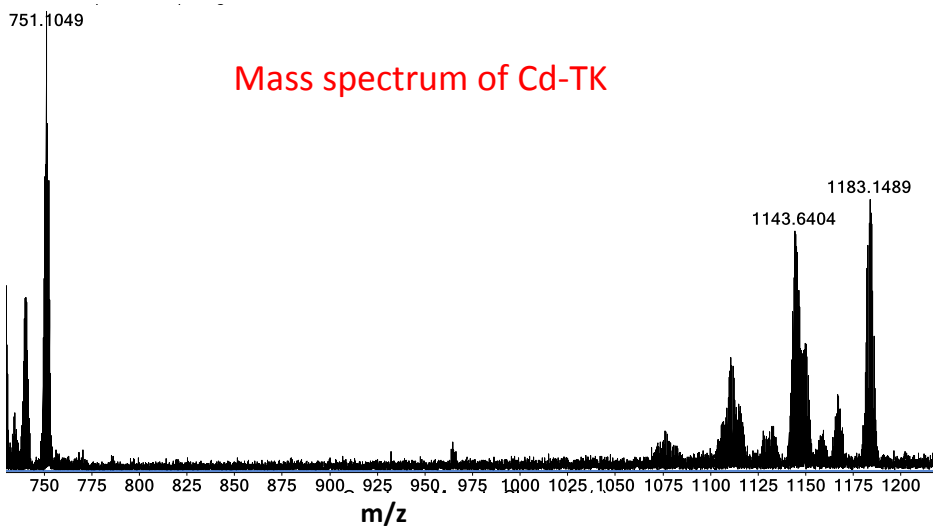


Figure S2. Full HR-MS spectra for Cd-TK, Cd-SL and Cd-[2]C samples and expansions of corresponding isotopic distribution patterns.

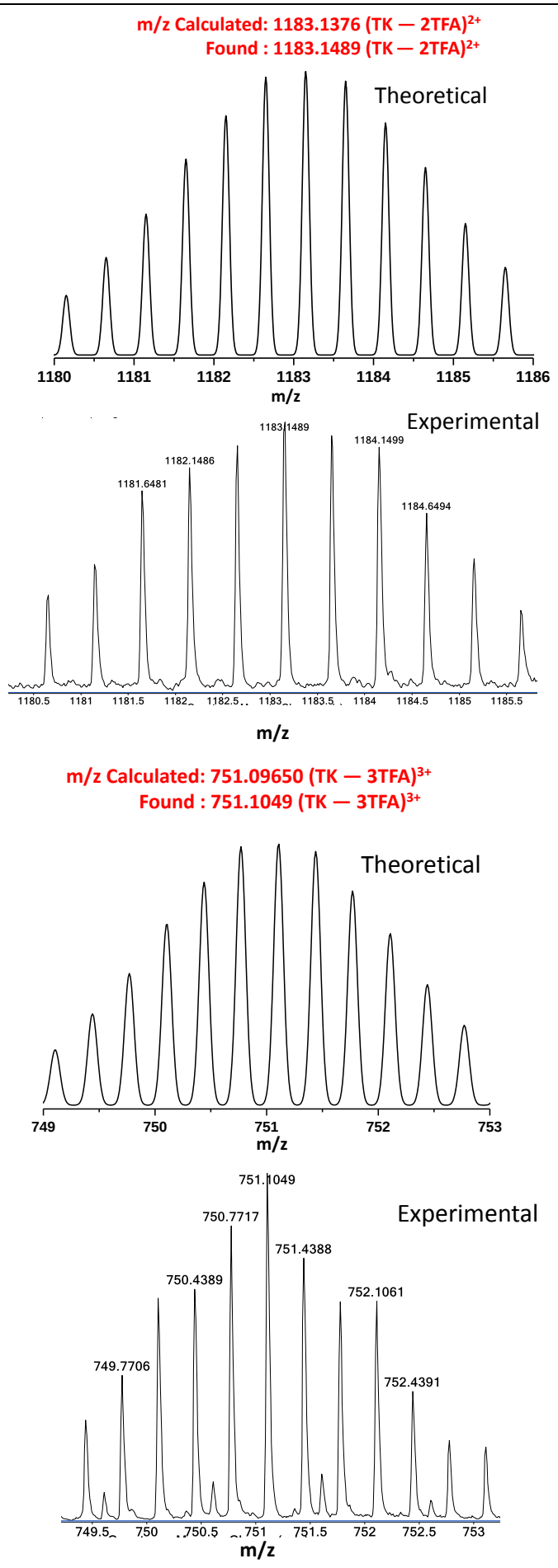
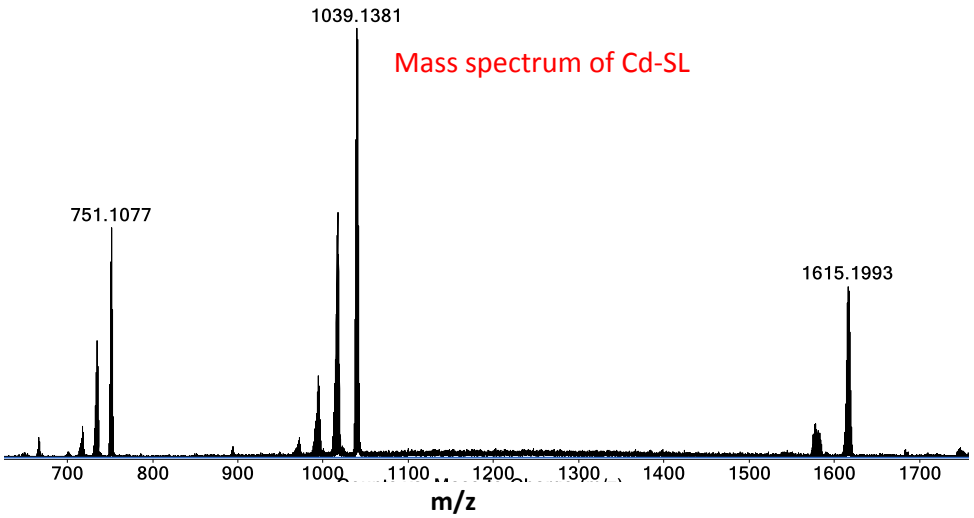


Figure S2. Full HR-MS spectra for Cd-TK, Cd-SL and Cd-[2]C samples and expansions of corresponding isotopic distribution patterns.



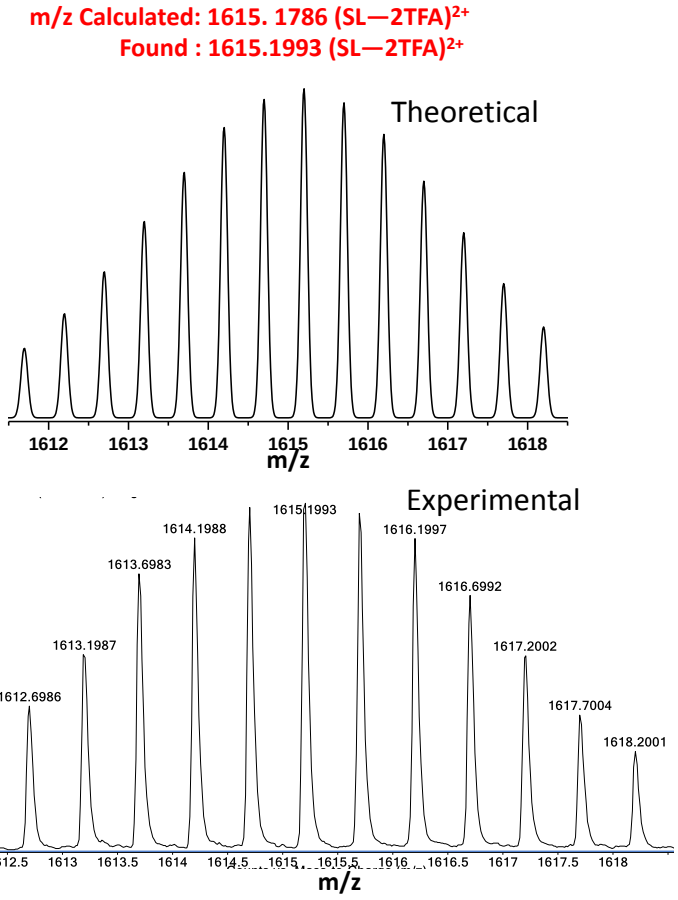
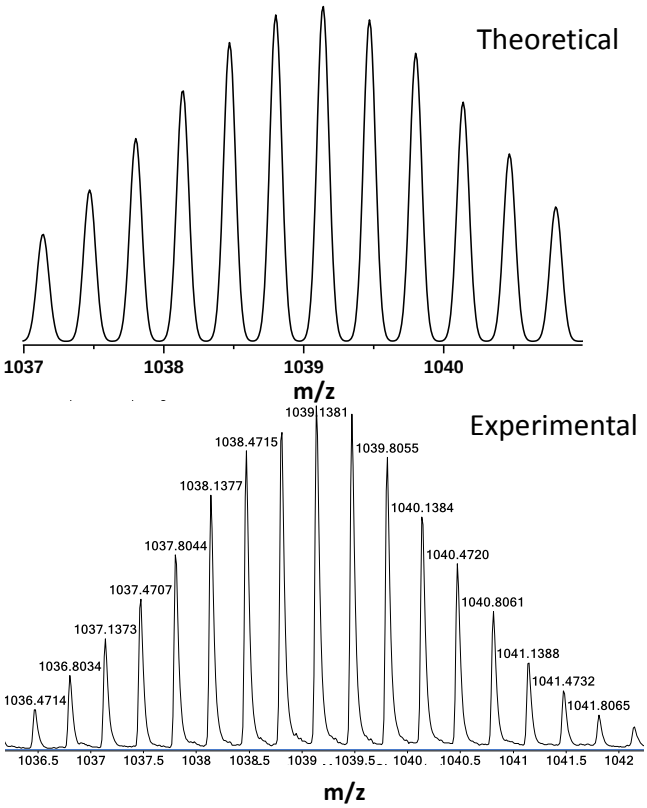
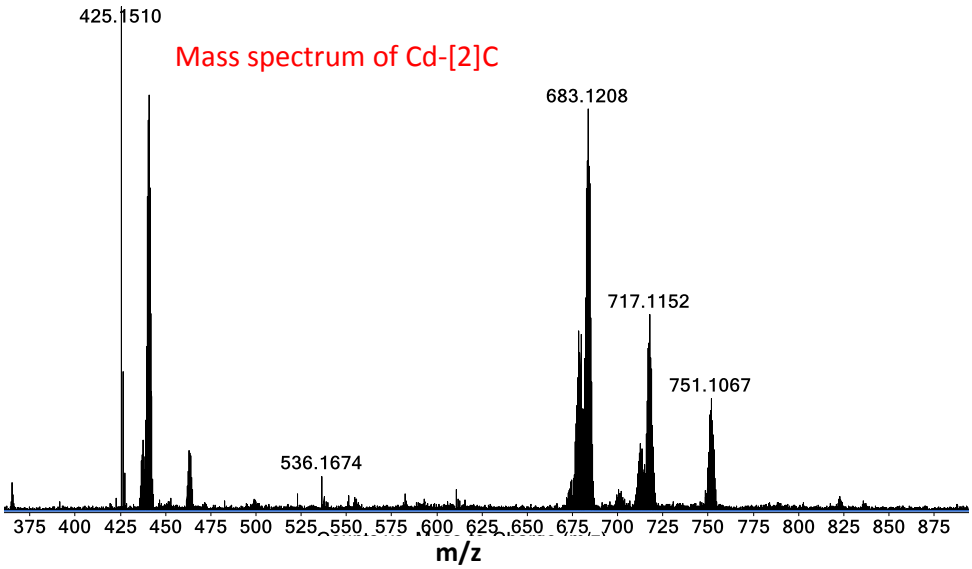


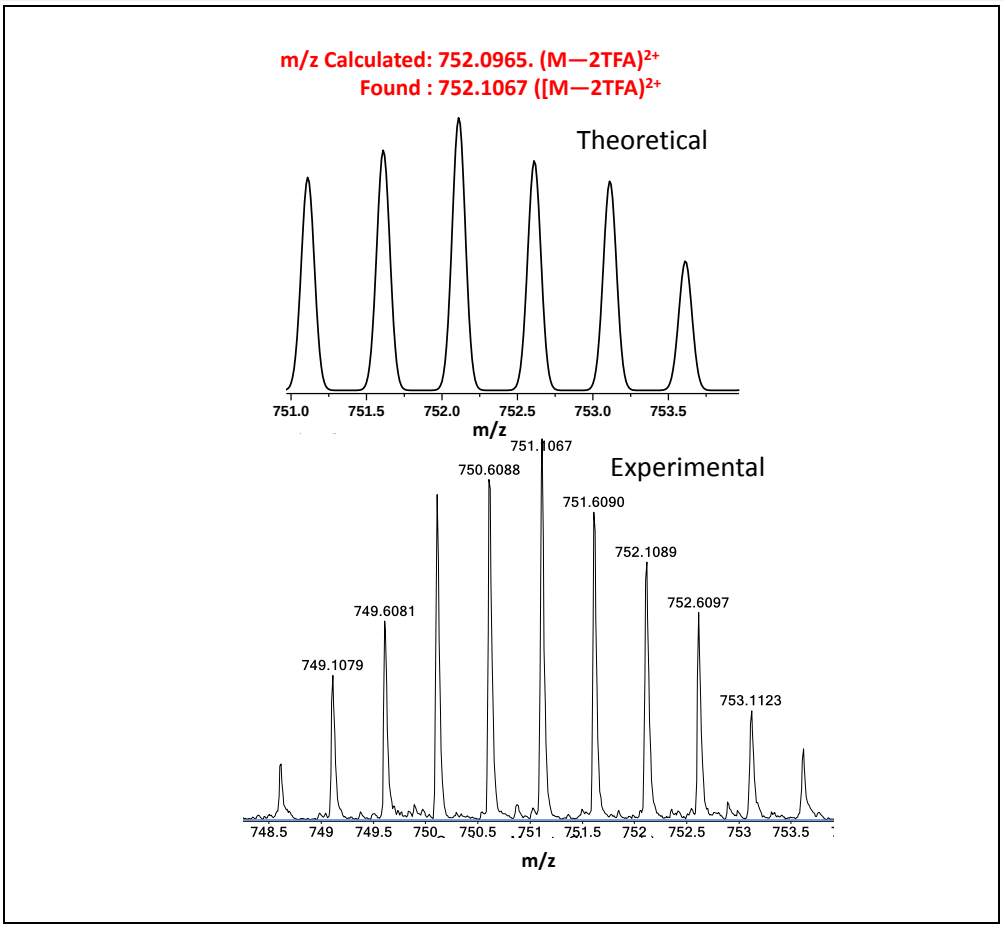
Figure S2. Full HR-MS spectra for Cd-TK, Cd-SL and Cd-[2]C samples and expansions of corresponding isotopic distribution patterns.

m/z Calculated: 1039.1239 $(SL—3TFA)^{3+}$

Found : 1039.1381 $(SL— 3TFA)^{3+}$







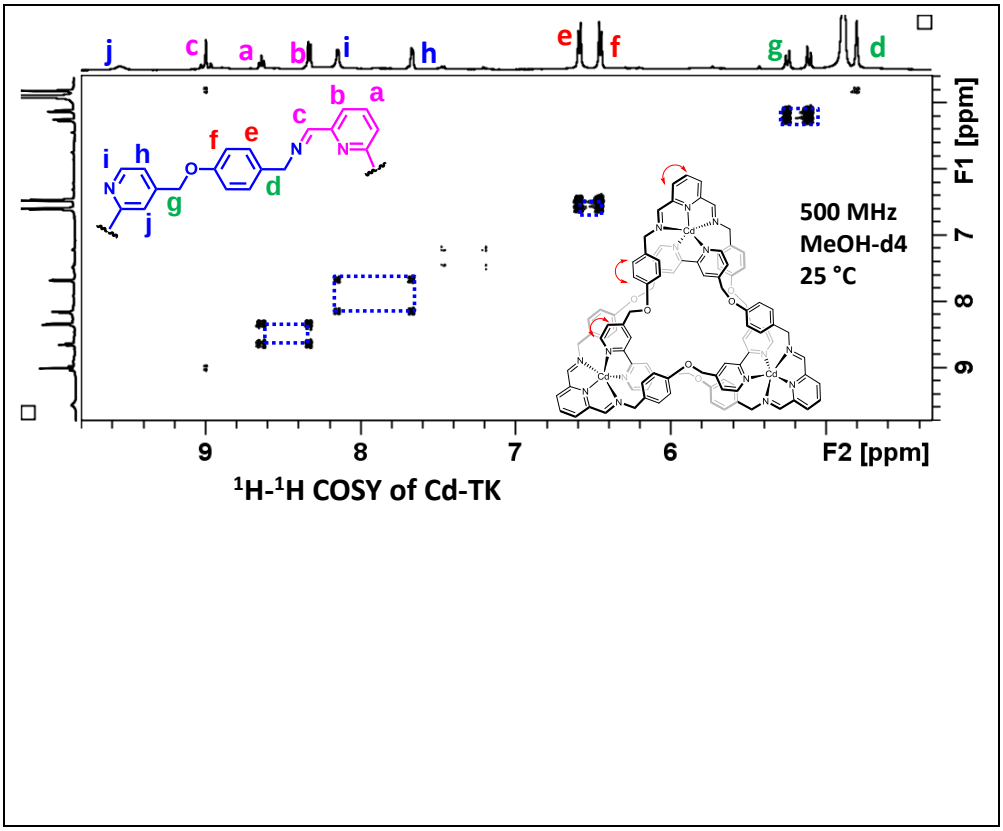
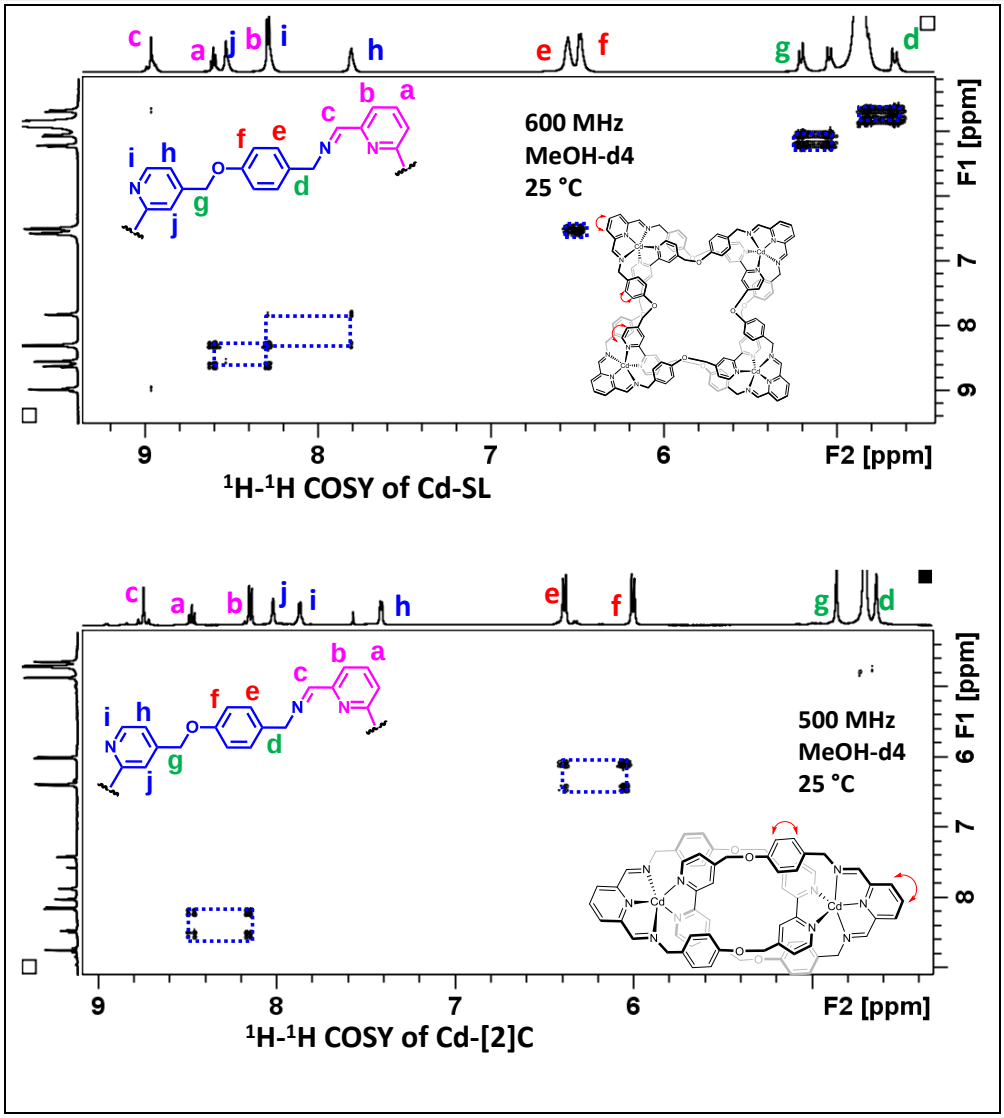


Figure S3. ^{1}H–^{1}H Gradient-selected double-quantum filtered phase-sensitive COSY NMR spectra (600 MHz) of Cd-TK, Cd-SL and Cd-[2]C in CD_3OD at 298 K.


c a j b i h e f g d
600 MHz
MeOH-d4
25 °C
F1 [ppm]
F2 [ppm]
9 8 7 6
^{1}H-^{1}H COSY of Cd-SL
c a b j i h e f g d
500 MHz
MeOH-d4
25 °C
F1 [ppm]
F2 [ppm]
9 8 7 6
^{1}H-^{1}H COSY of Cd-[2]C

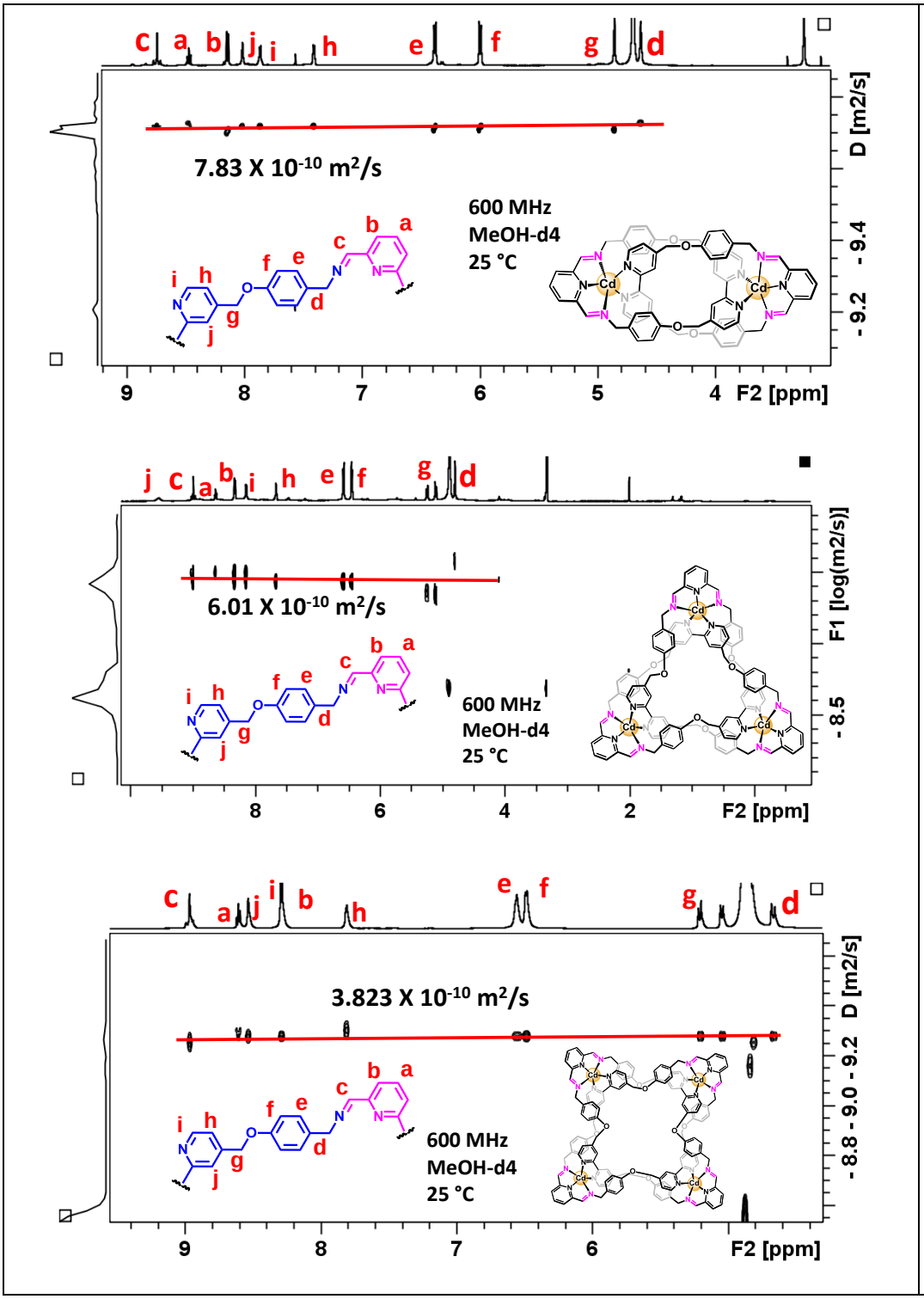
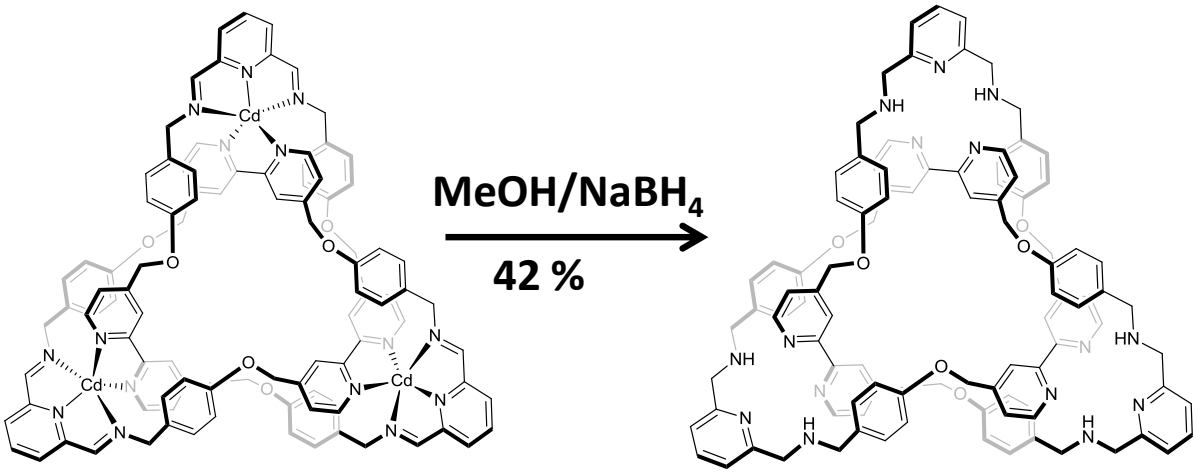


Figure S3a. ^{1}H DOSY NMR spectra of Cd-[2]C, Cd-TK, and Cd-SL MeOD-d4 at 298 K.

4. Demetalation of Cd-TK/ Synthesis of TK



A previously reported reduction procedure was followed.[3] Cd-TK (12.5 mg, 4.8 μmol 1 equiv.) was added to sodium borohydride (14.5 mg, 384 μmol, 40 equiv.) and dry MeOH (8 mL) in a 10 ml reaction flask. The mixture was stirred under nitrogen atmosphere at room temperature for 15 h. After reaction completion, the mixture was concentrated in a rotary evaporator. To remove unwanted sideproducts (linear chain fragments), acetonitrile (10 mL) was added, and the mixture was filtered. The filtrate was concentrated to dryness under vacuum for 6 h.

TK: 6.40 mg, 42 %; ^{1}H NMR (500 MHz, ACN-d3, 25 °C): δ 3.75 (brs, 12H, Ar-C*H*$_2$), 4.14 (d, 12H, *J* = 7.5 Hz, Ar-C*H*$_2$), 5.11 (ABq, 12H, *J* = 11.4 Hz, Ar-C*H*$_2$), 6.09 (brs, 6H, Ar-*H*), 6.39 (d, 12H, *J* = 8.2 Hz, Ar-*H*),), 6.53 (d, 12H, *J* = 7.9 Hz, Ar-*H*), 7.49 (d, 6H, *J* = 7.8 Hz, Ar-*H*), 8.04 (t, 3H, *J* = 7.8 Hz, Ar-*H*), 8.62 (brs, 6H, Ar-*H*), 9.52 (brs, 6H, Ar-*H*); ^{13}C NMR (125 MHz, ACN-d3, 25 °C): δ 51.7, 52.8, 68.1, 114.0, 116.6, 118.6, 120.6, 122.5, 129.6, 140.3, 148.9, 149.5, 150.6, 156.2, 157.4; MS (ESI-HRMS): m/z Calcd for $(C_{99}H_{96}N_{15}O_6)^{2+}$: 795.3806 $[M+2H]^{2+}$, found: 795.3860 $[M+2H]^{2+}$.

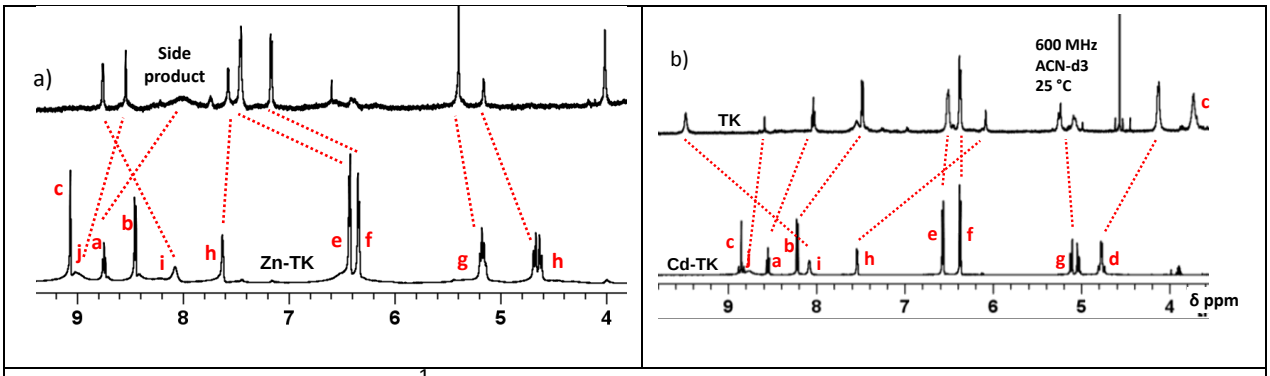


Figure S4. Stacked plots of ^{1}H NMR spectra corresponding to a) Zn-TK (bottom) and its reduction product (top) and b) Cd-TK (bottom) and TK (top), with all samples measured at 298 K in acetonitrile–d3.

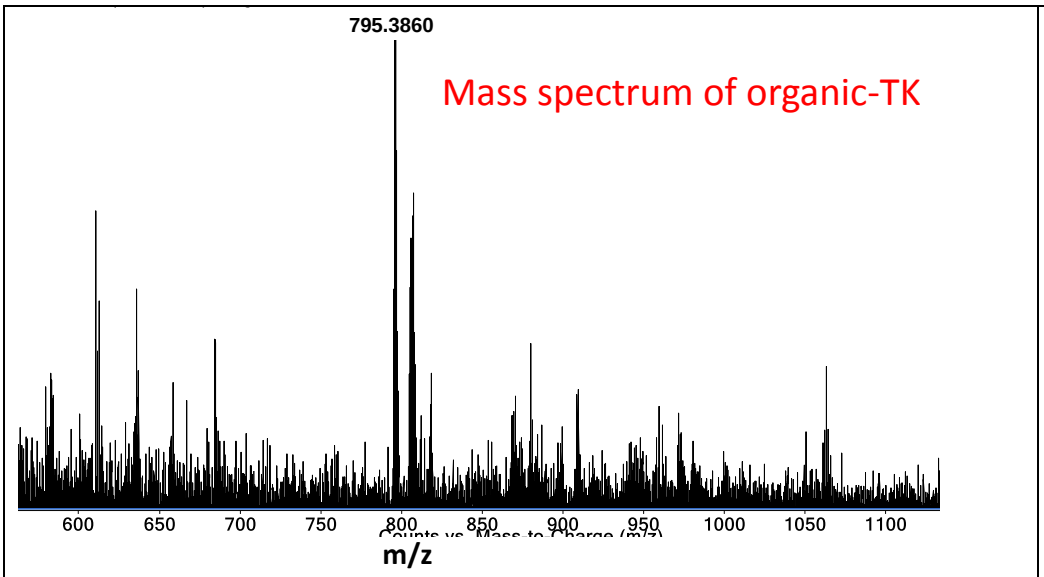
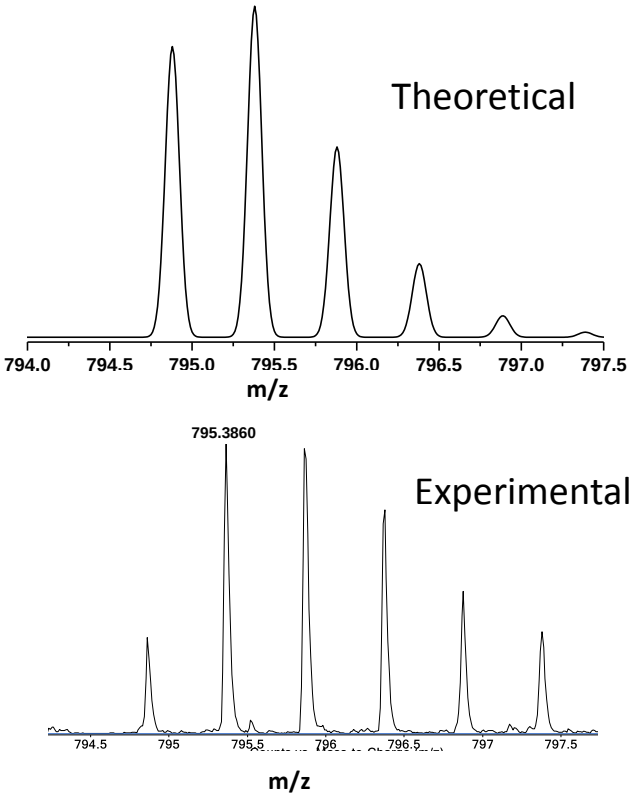
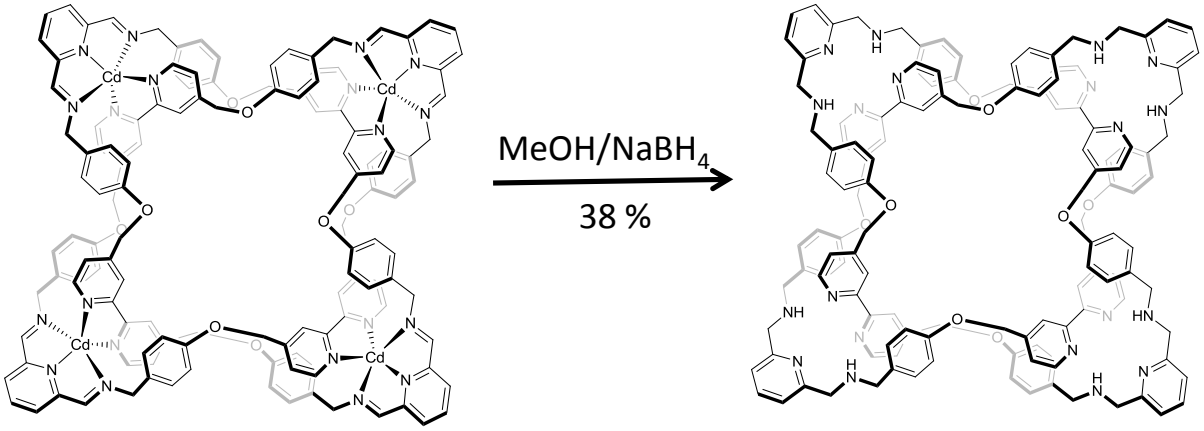


Figure S5. HR-MS spectrum of TK and expansions of isotopic distribution patterns of TK cations.



5. Demetalation of Cd-SL/ Synthesis of SL



The method described above for TK synthesis was adapted to produce SL, starting from 10 mg of Cd-SL.

SL: 2.3 mg, 38 %; ^{1}H NMR (500 MHz, ACN-d3, 25 °C): δ 3.33 (brs, 16H, Ar-CH_2), 3.50 (d, 16H, J = 9.0 Hz, Ar-CH_2), 4.80 (d, 16H, J = 11.4 Hz, Ar-CH_2), 6.44 (d, 16H, J = 8.3 Hz, Ar-H), 6.70 (d, 16H, J = 8.2 Hz, Ar-H), 7.06 (d, 8H, J = 7.6 Hz, Ar-H), 7.13 (brs, 8H, Ar-H), 7.56 (t, 4H, J = 7.7 Hz, Ar-H), 8.08 (brs, 8H, Ar-H), 8.37 (brs, 8H, Ar-H); ^{13}C NMR (125 MHz, ACN-

d3, 25 °C): δ 53.8, 55.2, 68.9, 115.6, 117.5, 120.0, 121.8, 123.2, 130.7, 133.8, 138.5, 149.0, 150.6, 157.0, 158.0; MS (ESI-HRMS): m/z Calcd for $(C_{132}H_{128}N_{20}O_8)^{2+}$: 1060.5045 $[M+2H]^{2+}$, found: 1060.5054 $[M+2H]^{2+}$, m/z Calcd for $(C_{132}H_{130}N_{20}O_8)^{4+}$: 530.7560 $[M+4H]^{4+}$, found: 530.7572 $[M+4H]^{4+}$.

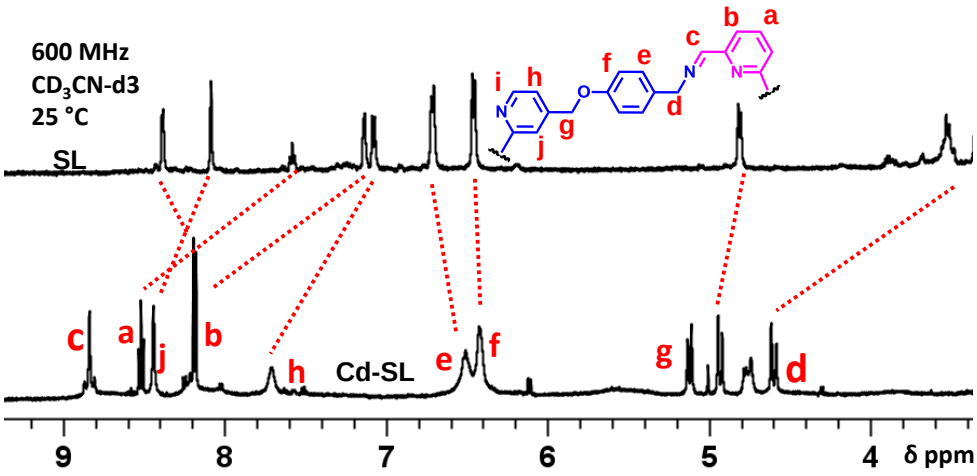


Figure S6. Stacked plots of ^{1}H NMR spectra of Cd-SL and SL in acetonitrile–d3 at 298 K.

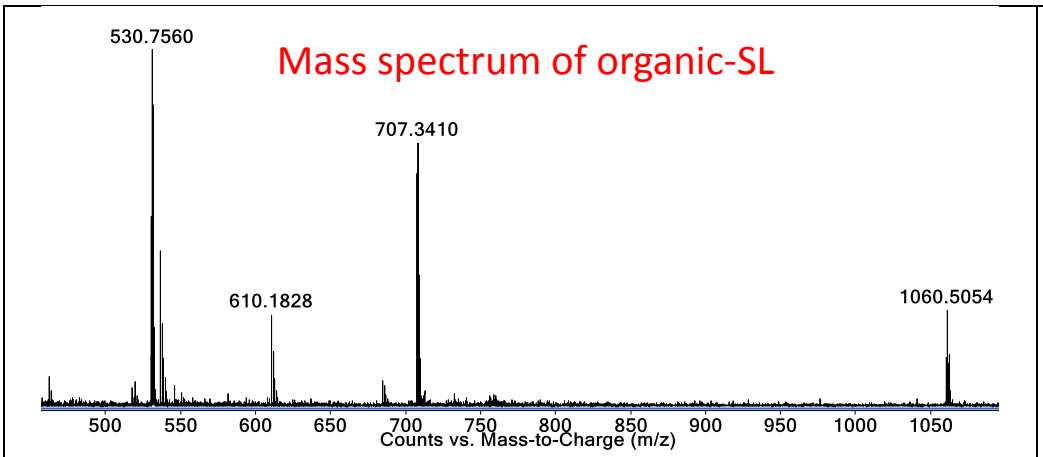
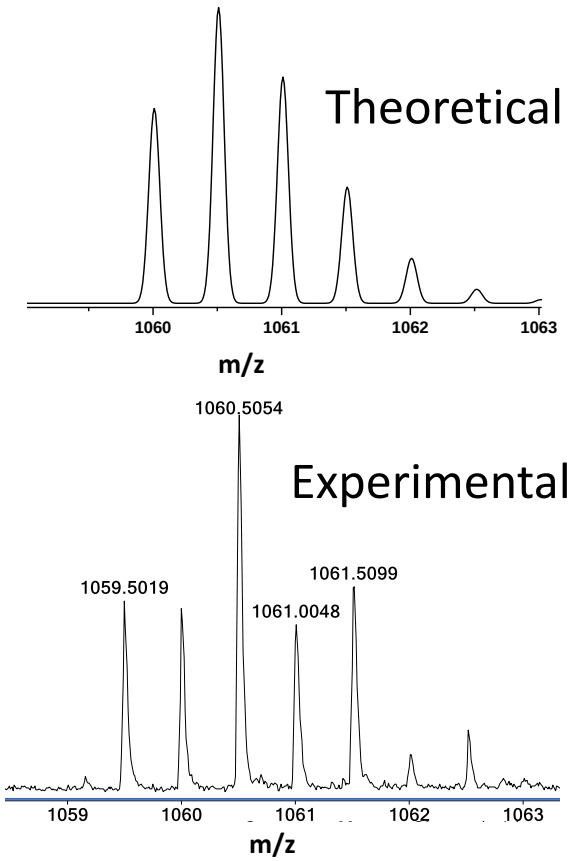
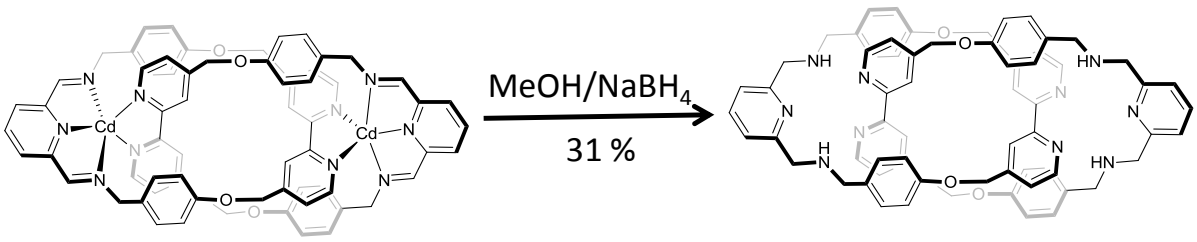


Figure S7. Mass spectrum of SL and expansions of isotopic distribution patterns of SL cations.

m/z Calculated : 1060.5045 $[M+2H]^{2+}$
Found : 1060.5054 $[M+2H]^{2+}$



6. Demetalation of Cd-[2]C/ Synthesis of [2]C



To a 10 ml round bottom flask containing Cd-[2]C (10mg, 5.7 µmol 1 equiv.) was added sodium borohydride (8.7 mg, 228 µmol, 40 equiv.) and dry MeOH (5 mL). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 16 h. The mixture was concentrated to dryness and acetonitrile (4 mL) was added. The mixture was filtered, and the filtrate was

concentrated and dried under vacuum for 4 h. The solid obtained was characterized by NMR spectroscopy and mass spectrometry.

[2]C: 1.89 mg, 31 %; ^{1}H NMR (500 MHz, ACN-d3, 25 °C): δ 3.86 (q, *J* = 6.1 Hz, 16H, Ar-C*H*$_2$), 5.31 (s, 8H, Ar-C*H*$_2$), 6.45 (brs, 16H, Ar-*H*),), 7.51 (brs, 4H, Ar-*H*), 7.61 (t, *J* = 3.7 Hz, 2H, Ar-*H*), 7.62 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 8.34 (brs, 4H, Ar-*H*), 8.74 (d, 4H, *J* = 4.9 Hz, Ar-*H*); ^{13}C NMR (125 MHz, ACN-d3, 25 °C): δ 48.8, 63.0, 66.9, 114.8, 119.7, 121.0, 123.0, 129.5, 136.7, 137.6, 148.6, 149.9, 156.0, 156.8, 158.4; MS (ESI-HRMS): m/z Calcd for $(C_{66}H_{66}N_{10}O_4)^{2+}$: 531.2628 $[M+2H]^{2+}$, found: 531.2615 $[M+2H]^{2+}$.

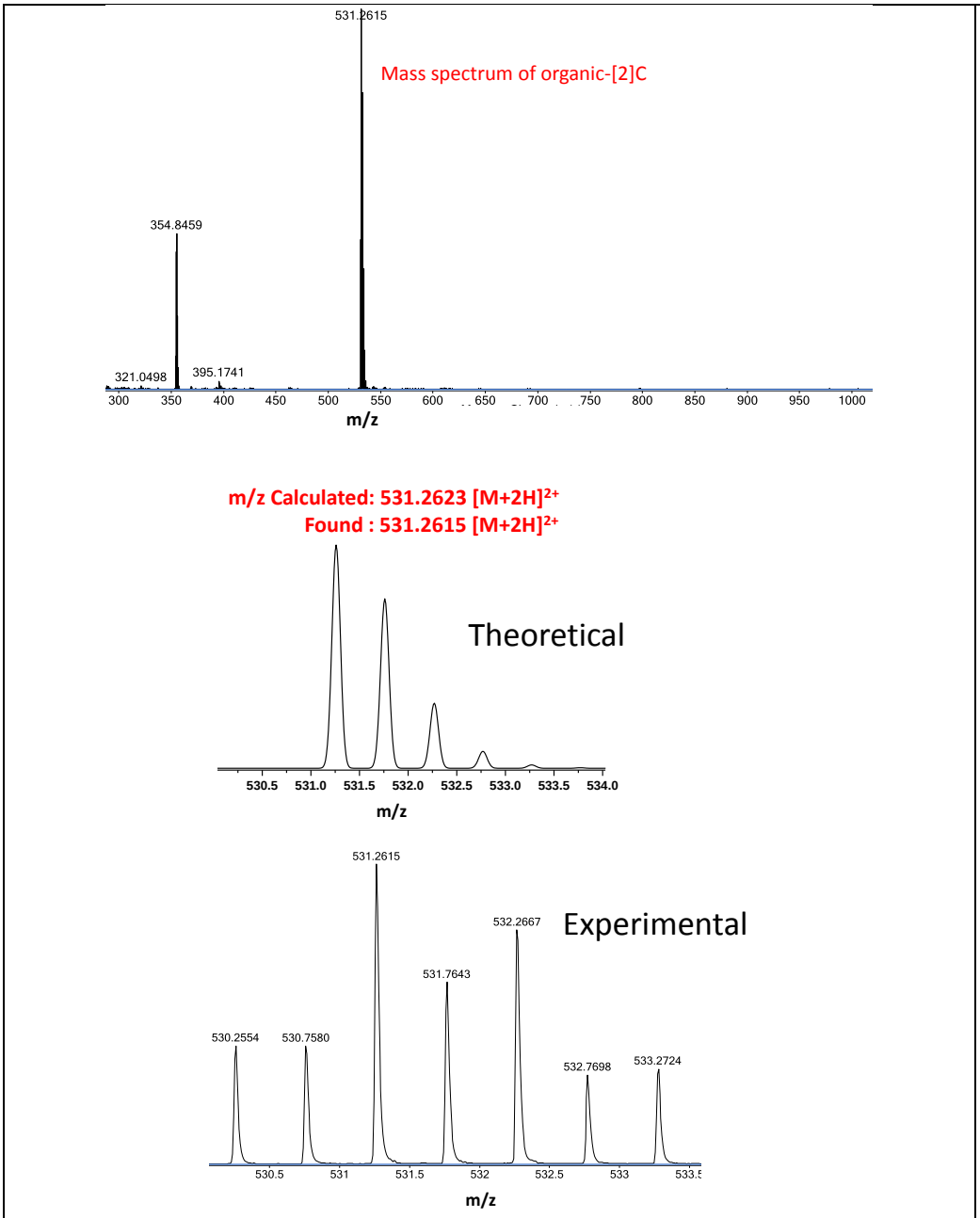


Figure S8. Mass spectrum of [2]C and corresponding expanded isotopic distribution patterns.

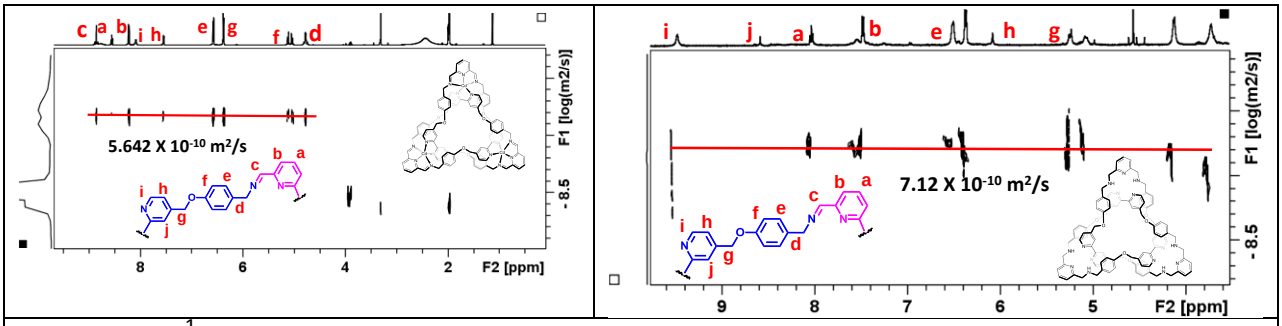


Figure S9. ^{1}H DOSY NMR spectra (600 MHz) of Cd-TK (left) and TK (right) in CD_3CN–d3 at 298 K.

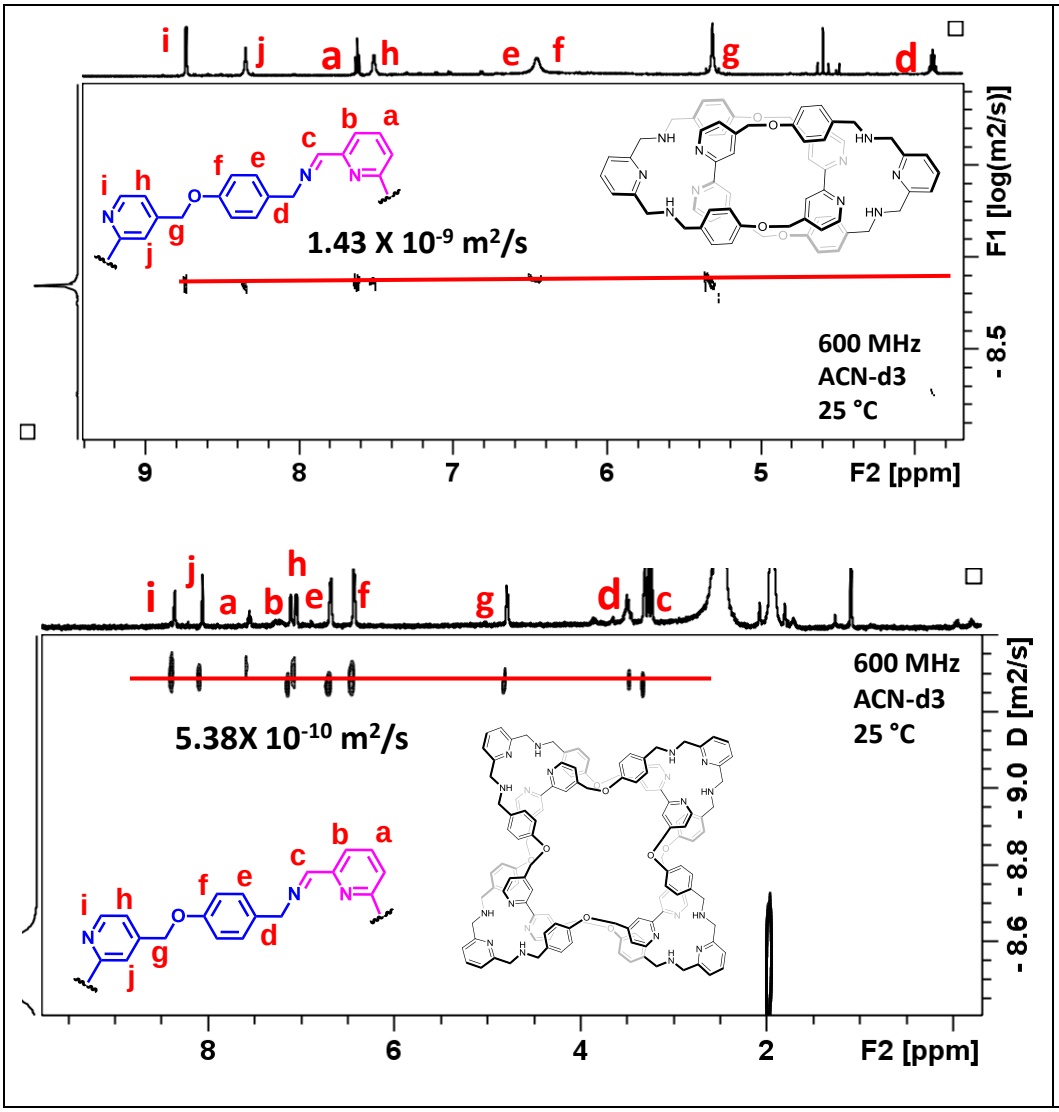


Figure S10. ^{1}H DOSY NMR spectra (600 MHz) of SK and [2]C in acetonitrile–d3 at 298 K.

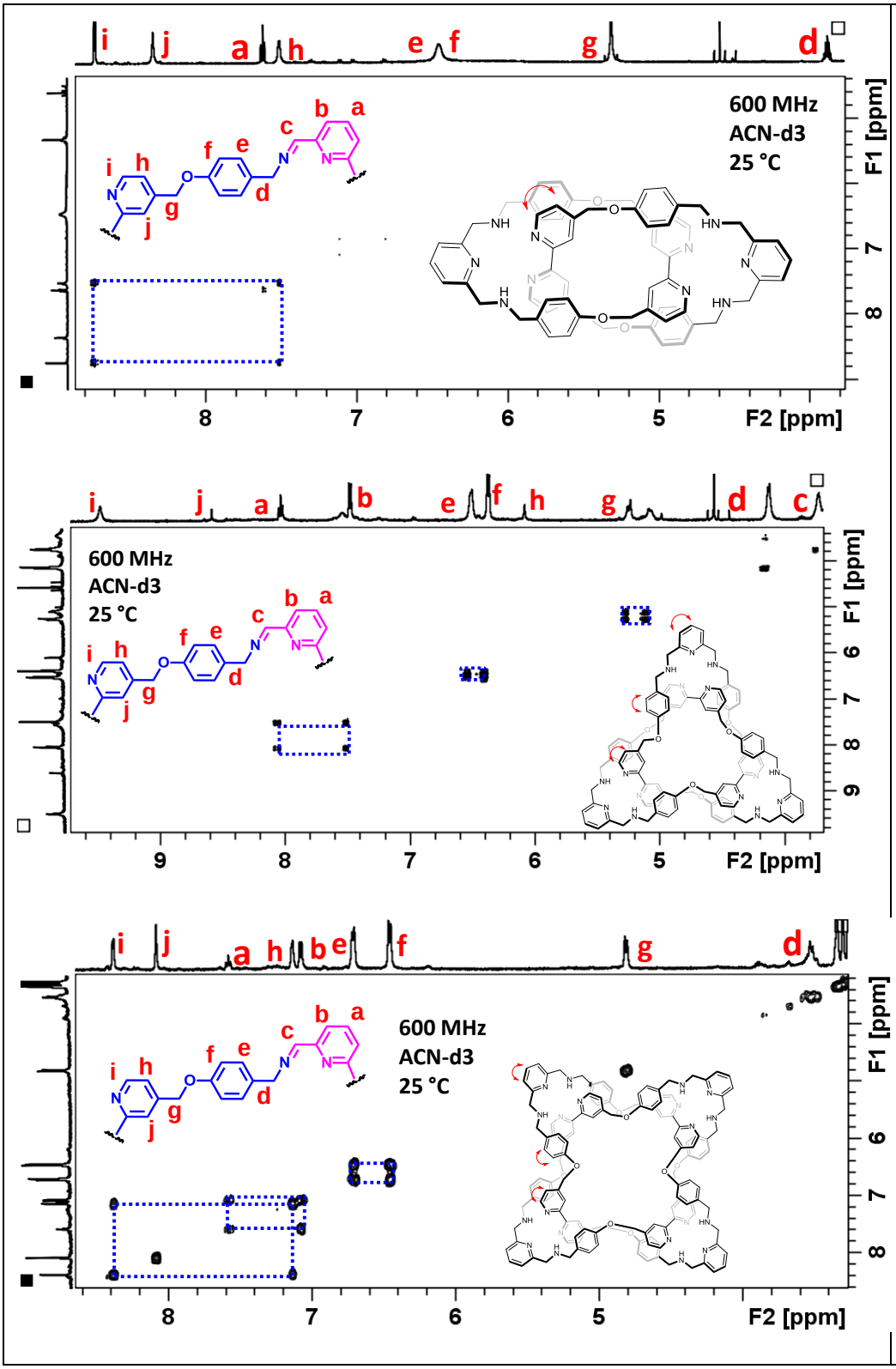
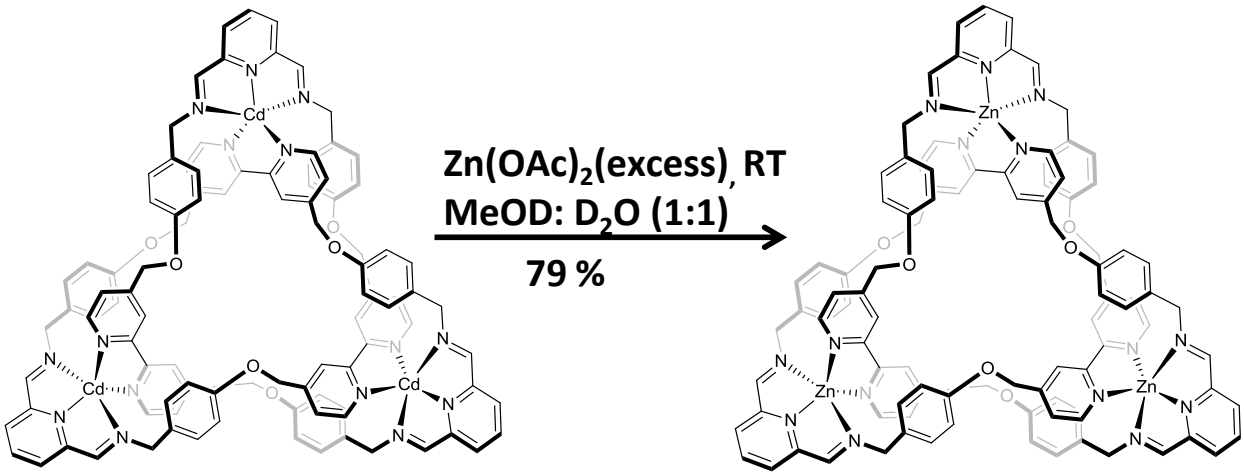


Figure S11. ^{1}H–^{1}H gradient-selected double-quantum filtered phase-sensitive COSY NMR spectra (600 MHz) of TK, SL and [2]C in ACN-d3 at 298 K.

7. Transmetalation of Cd-TK with zinc acetate



Cd-TK (6 mg) was added to different amounts of zinc acetate (1, 2, 3, 5, 10, and 20 equivalents) in a 1:1 mixture of deuterated methanol and water. The samples were prepared in NMR tubes at room temperature and the progress of the reactions was monitored by ^{1}H NMR spectroscopy. Transmetalation of cadmium was fastest with 20 equivalents of zinc acetate, leading to 79% conversion to Zn-TK in one day. Greater amounts of zinc acetate lead to unwanted side reactions. After reaction completion, Zn-TK was precipitated with isopropanol and the precipitate washed 3-4 times with hot isopropanol to remove open chain zinc complexes and excess of zinc acetate. The precipitate was finally dried under vacuum for 4 h.

Zn-TK: 4.5 mg, 79%; ^{1}H NMR (500 MHz, MeOH-d4, 25 °C): δ 4.68 (d, 12H, *J* = 14.6 Hz, Ar-C*H*$_2$), 5.11 (d, 12H, *J* = 7.2 Hz, Ar-C*H*$_2$), 6.44 (d, 12H, *J* = 8.6 Hz, Ar-*H*), 6.56 (d, 12H, *J* = 8.7 Hz, Ar-*H*), 7.67 (d, 6H, *J* = 5.3 Hz, Ar-*H*), 8.13 (d, 6H, *J* = 5.3 Hz, Ar-*H*), 8.41 (d, 6H, *J* = 7.9 Hz, Ar-*H*), 8.59 (brs, 6H, Ar-*H*), 8.70 (t, 3H, *J* = 7.9 Hz, Ar-*H*), 8.97 (brs, 6H, Ar-*H*); ^{13}C NMR (75 MHz, MeOD-d4, 25 °C): δ; 61.2, 67.4, 115.5, 116.8 (q, $^{2}J_{C\text{-}F}$ = 292.5 Hz, TFA), 124.3, 126.2, 127.9, 128.9 130.2, 130.5, 147.1, 148.4, 149.0, 158.1, 158.6, 160.2, 161.32 (q, $^{3}J_{C\text{-}F}$ = 34.5 Hz. TFA). MS (ESI-HRMS): m/z Calcd for $(C_{107}H_{85}F_{12}N_{15}O_{14}Zn_3)^{2+}$: 1111.7006 [TK−2TFA]$^{2+}$, found: 1111.6903 [TK−2TFA]$^{2+}$, m/z Calcd for $(C_{105}H_{87}F_9N_{15}O_{12}Zn_3)^{3+}$: 704.1357 [TK−3TFA]$^{3+}$, found: 704.1332 [TK−3TFA]$^{3+}$.

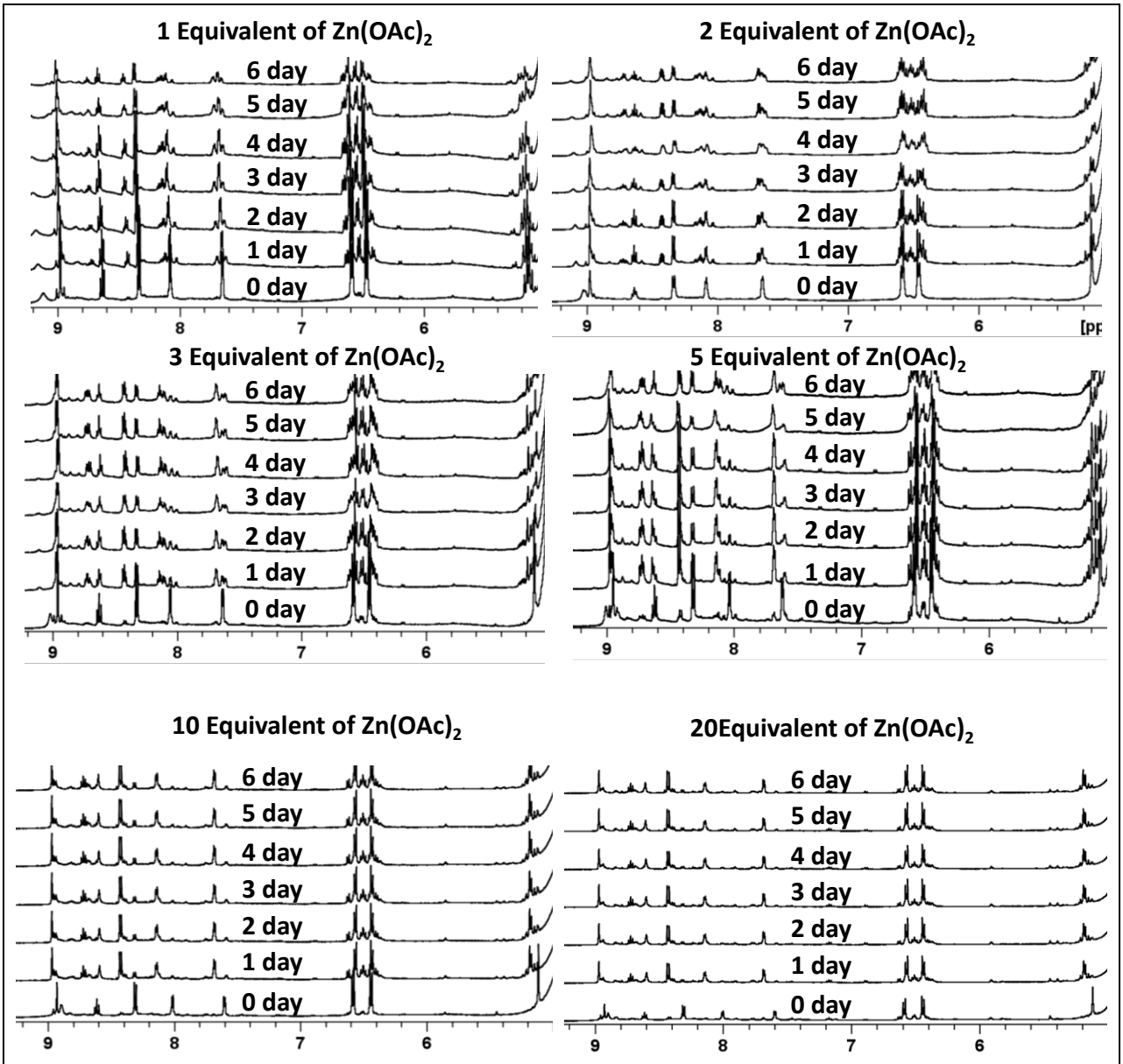
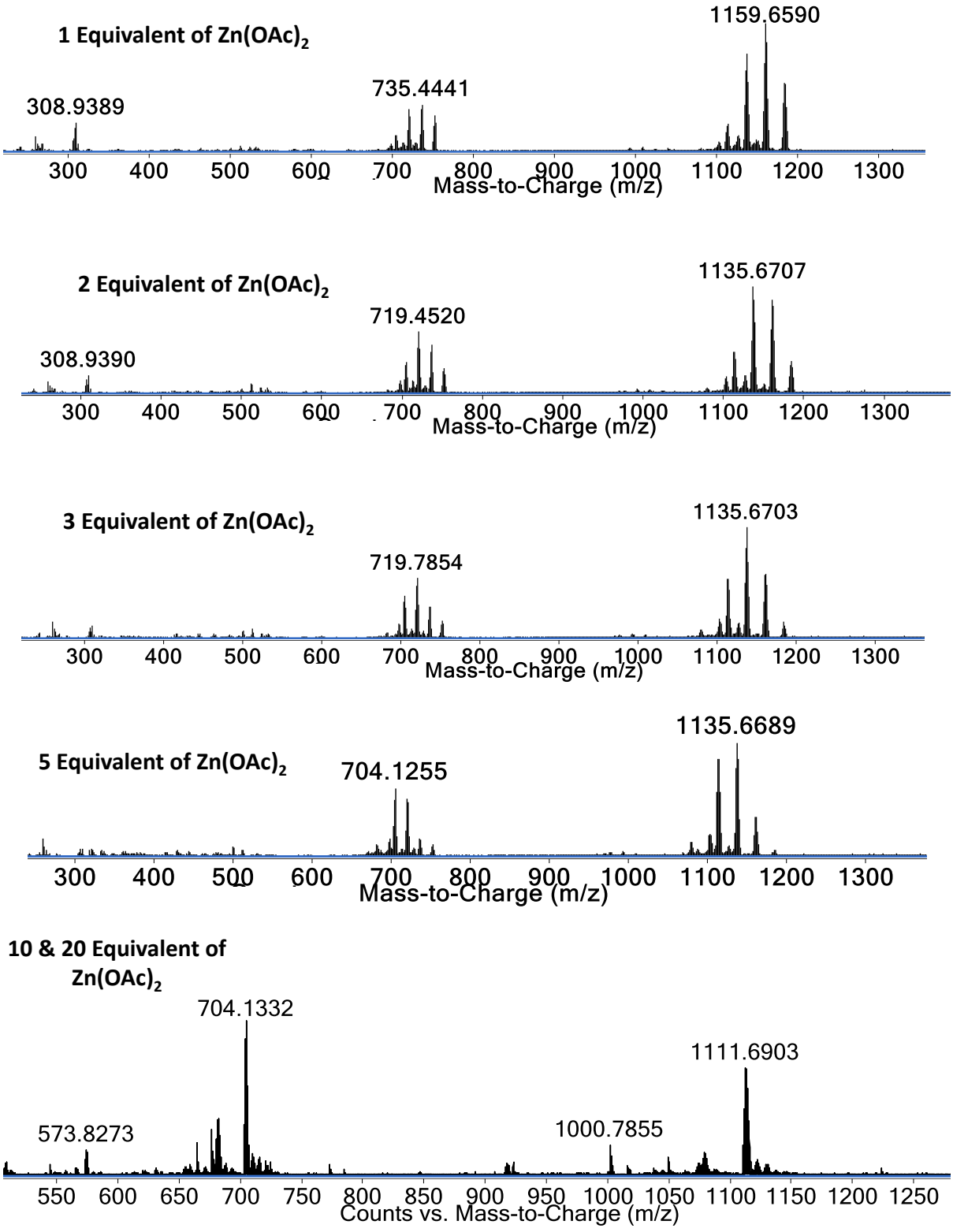


Figure S12a. ^{1}H NMR spectroscopic monitoring at 500 MHz of the transmetalation of Cd-TK with varied amounts of $Zn(OAc)_2$ in D_2O/MeOD-d4 (1:1) mixtures at 298 K.

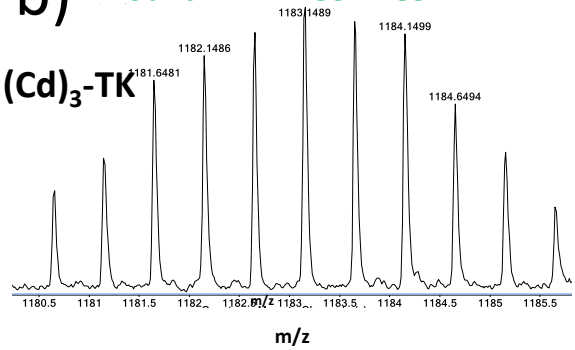
a)


1 Equivalent of Zn(OAc)2
1159.6590
735.4441
308.9389
300 400 500 600 700 800 900 1000 1100 1200 1300
Mass-to-Charge (m/z)
2 Equivalent of Zn(OAc)2
1135.6707
719.4520
308.9390
300 400 500 600 700 800 900 1000 1100 1200 1300
Mass-to-Charge (m/z)
3 Equivalent of Zn(OAc)2
1135.6703
719.7854
300 400 500 600 700 800 900 1000 1100 1200 1300
Mass-to-Charge (m/z)
5 Equivalent of Zn(OAc)2
1135.6689
704.1255
300 400 500 600 700 800 900 1000 1100 1200 1300
Mass-to-Charge (m/z)
10 & 20 Equivalent of Zn(OAc)2
704.1332
1111.6903
573.8273
1000.7855
550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250
Counts vs. Mass-to-Charge (m/z)

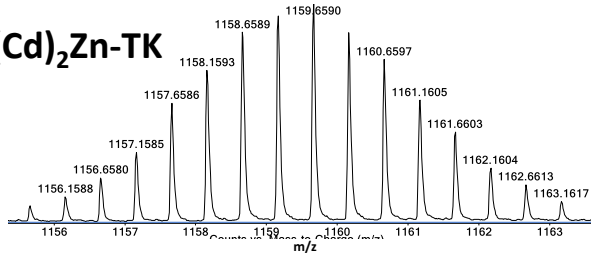
$(M—2TFA)^{2+}$

b)

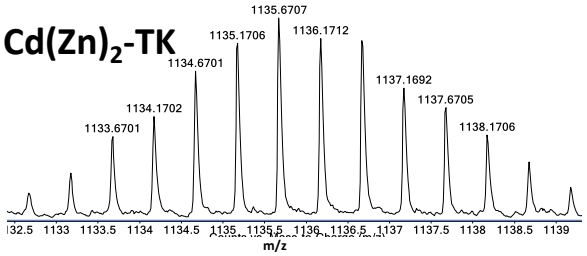
Calculated:1183.1376
Found : 1183.1489



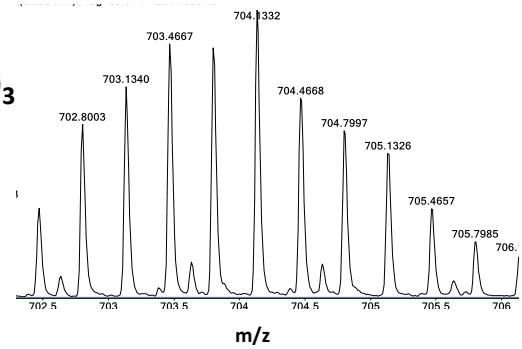
Calculated: 1159.6627
Found : 1159.6590



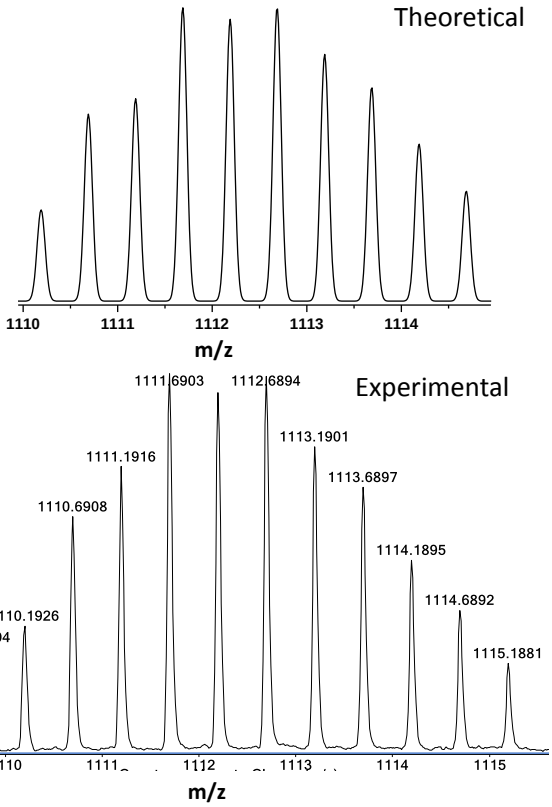
Calculated: 1135.6840
Found : 1135.6707



Calculated: 1111.7006
Found : 1111.6903



m/z Calculated: 1111.7006 $(M—2TFA)^{2+}$
Found : 1111.6903 $(M—2TFA)^{2+}$



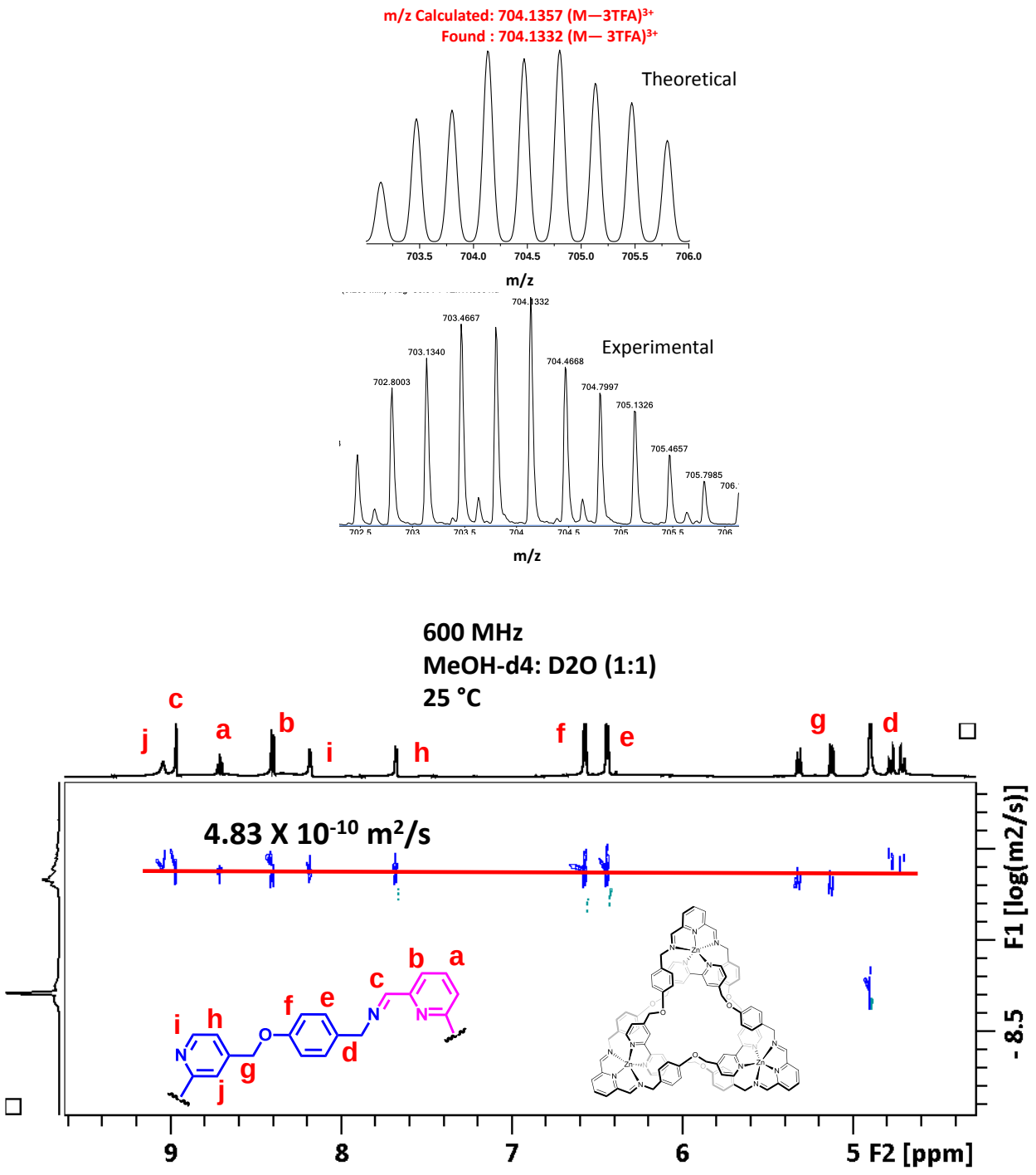
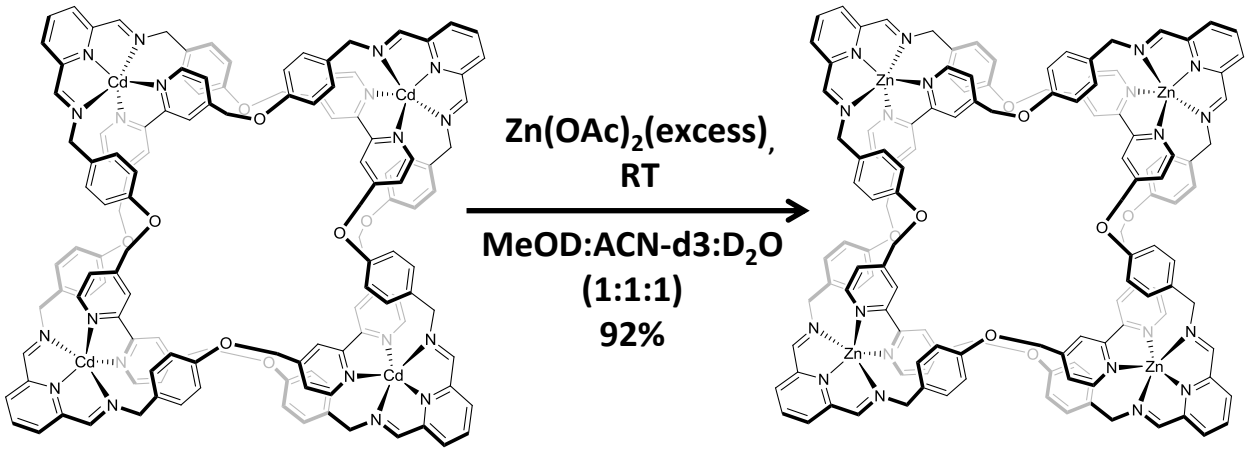


Figure S12b. (a) HR-MS analysis of Cd-TK samples having different molar amounts of $Zn(OAc)_2$. (b) Isotopic distribution patterns corresponding to $(Cd)_3$-TK, $(Cd)_2Zn$-TK, $Cd(Zn)_2TK$ and $(Zn)_3$-TK species.

8. Transmetalation of Cd-SL with zinc acetate



Cd-SL (10 mg) was added to an excess of zinc acetate in a 1:1:1 mixture of MeOD, CD_3CN and D_2O. The reaction was complete five minutes after zinc acetate addition, yielding Zn-SL as the major product. The mixture was concentrated to dryness and isopropanol was added. Zn-SL was collected by filtration and dried under vacuum for 4 h.

Zn-SL: 8.6 mg, 92%; ^{1}H NMR (500 MHz, MeOH-d4, D_2O and CD_3CN, 25 °C): δ 4.59 (ABq, 16H, *J* = 14.6 Hz, Ar-C*H*$_2$), 4.98 (ABq, 16H, *J* = 14.5 Hz, Ar-C*H*$_2$), 6.37 (ABq, 32H, *J* = 7.6 Hz, Ar-*H*), 7.62 (brs, 8H, Ar-*H*), 8.11 (brs, 8H, Ar-*H*), 8.16 (d, 8H, *J* = 7.8 Hz, Ar-*H*), 8.47 (brs, 8H, Ar-*H*), 8.49 (t, 4H, *J* = 7.8 Hz, Ar-*H*), 8.80 (brs, 8H, Ar-*H*); ^{13}C NMR (125 MHz, MeOH-d4, D_2O and CD_3CN, 25 °C): δ 60.8, 67.7, 114.3, 115.9, 120.5 (q, $^2J_{C\text{-}F}$ = 272 Hz, TFA), 124.1, 125.0, 129.1, 129.3, 129.5, 129.9, 143.3, 147.5, 148.3, 149.0, 157.9, 160.6 (q, $^3J_{C\text{-}F}$ 8 35.7 Hz. TFA); MS (ESI-LRMS): m/z MS (ESI-HRMS): m/z Calcd for $(C_{142}H_{115}F_{15}N_{20}O_{18}Zn_4)^{3+}$: 976.1869 $[M-3TFA]^{3+}$, found: 976.1799 $[M-3TFA]^{3+}$.

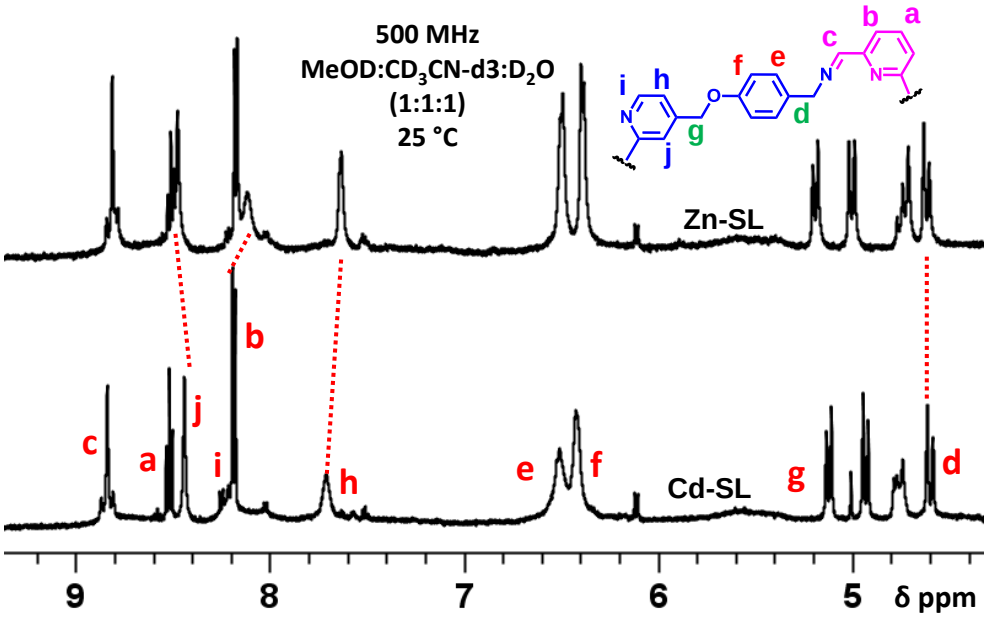


Figure S13. Stacked plot of ^{1}H NMR spectra of Cd-SL and Zn-SL in MeOD, CD_3CN and D_2O (1:1:1) mixture at 298 K.

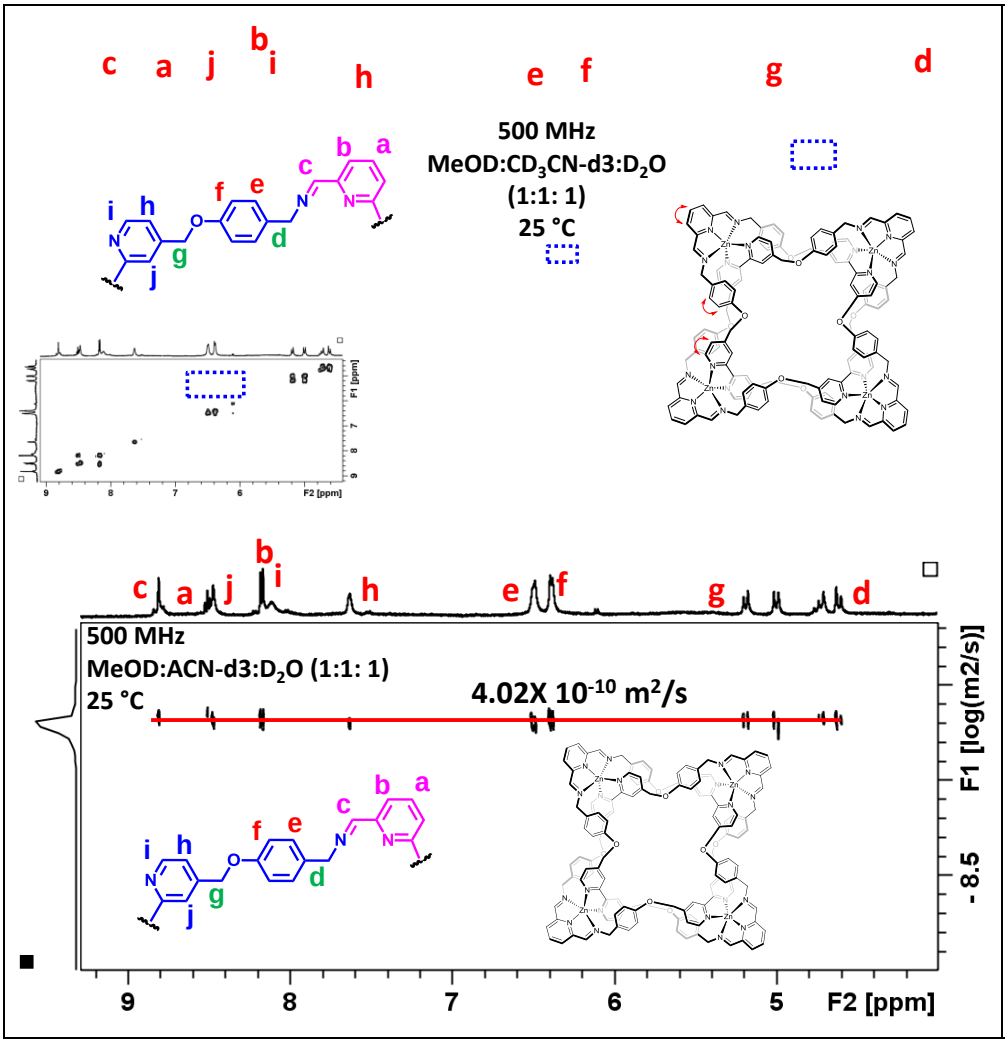


Figure S14. ^{1}H–^{1}H gradient-selected double-quantum filtered phase-sensitive COSY and ^{1}H DOSY NMR of Zn-SL in a MeOD, CD_3CN and D_2O (1:1:1) mixture at 298 K (600 MHz).

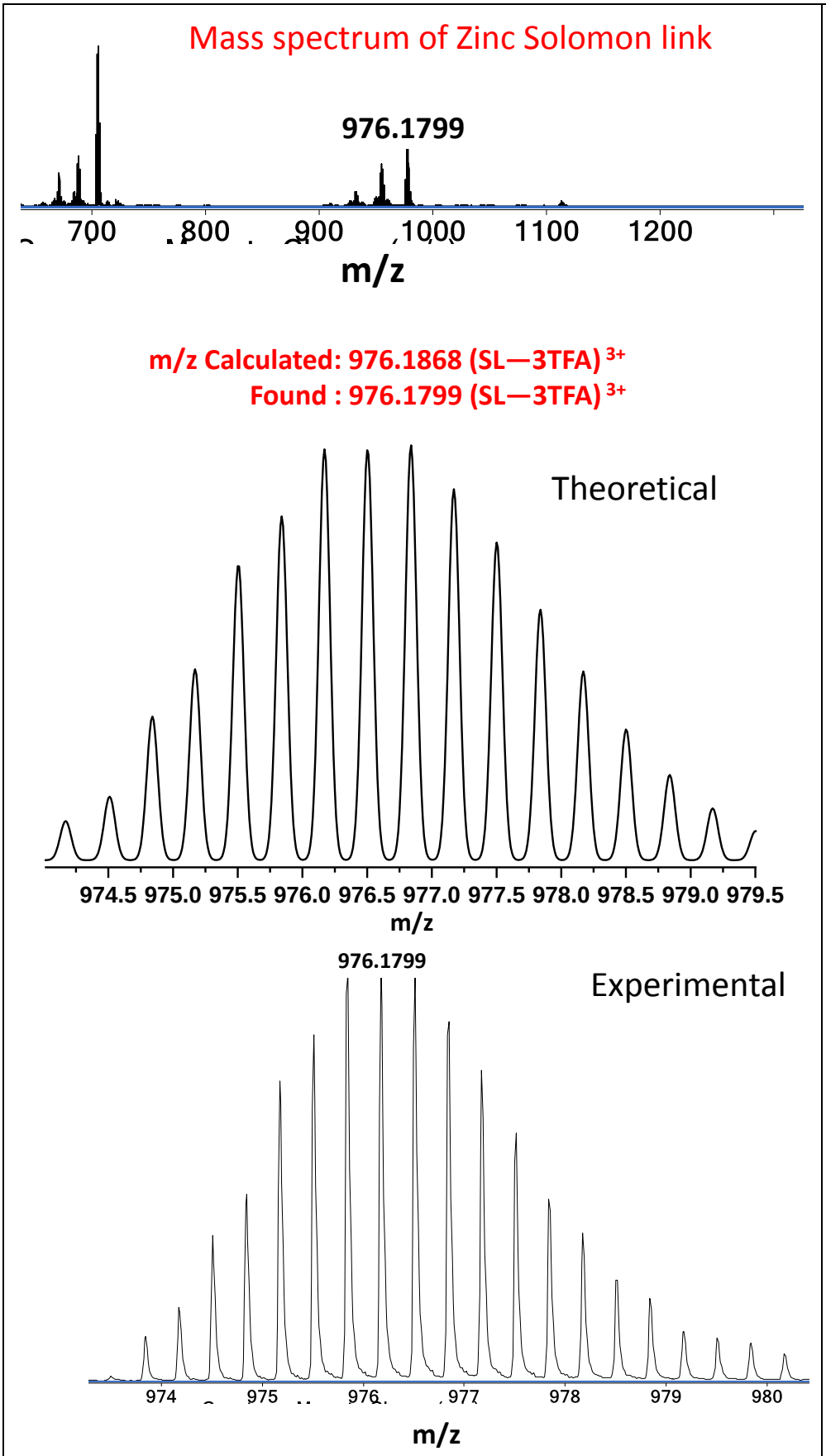


Figure S15. HR-MS spectra of Zn-SL and isotopic distribution pattern of Zn-SL cations.

9. Crystallographic characterization of Cd-[2]C, Cd-TK and Cd-SL

X-ray diffraction data for Cd-[2]C, Cd-TK and Cd-SL were collected at 100 K on a Bruker APEX II DUO and on a Bruker D8 QUEST diffractometer, respectively. Data reduction was performed with the Bruker Apex suite whereas crystal solution was obtained by direct methods using SHELL-X software via the X-Seed interface and then refined against all the Fobs. Residual electron density was "squeezed" out of the reflection intensity files with the PLATON suite prior the final refinement.[4]

Cd-[2]C: $C_{70}H_{56}BCd_2F_4N_{10}O_8$, M = 1476.85, yellow prism, 0.100 × 0.050 × 0.050 mm^3, orthorombic, space group *Ibam* (No. 72), V = 8197.9(6) Å^3, Z = 4, D_c = 1.197 g/cm^3, F_{000} = 2988, Bruker Apex II duo, CuKα radiation, λ = 1.54178 Å, T = 100(2)K, $2\theta_{max}$ = 140.5º, 40162 reflections collected, 3953 unique (R_{int} = 0.1023). Final *GooF* = 1.449, *R1* = 0.0614, *wR2* = 0.2078, *R* indices based on 3116 reflections with I I > 2(I) (refinement on F^2), 282 parameters, 5 restraints. Lp and absorption corrections applied, μ = 4.661 mm^{-1}.

Detailed X-ray crystal structure determination data for Cd-[2]C are available in the Cambridge crystallography data center (CCDC), with the deposition number **CCDC 1421589**. All crystallographic data are available free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C Cd_2C

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No syntax errors found. CIF dictionary Interpreting this report

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Bond precision:    C-C = 0.0058 A          Wavelength=1.54178

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                alpha=90         beta=90          gamma=90
 Temperature:   100 K
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Hall group	-I 2 2c	-I 2 2c
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Sum formula	C70 H56 B Cd2 F4 N10 O8	C70 H56 B Cd2 F4 N10 O8
Mr	1476.88	1476.85
Dx,g cm-3	1.197	1.197
Z	4	4
Mu (mm-1)	4.661	4.661
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F000'	2997.84	
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Tmin'	0.627	

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AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 70.268

R(reflections)= 0.0614(3116) wR2(reflections)= 0.2219(3953)

S = 1.449 Npar= 282

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

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Alert level C

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PLAT222_ALERT_3_C Non-Solvent Resd 1 H Uiso(max)/Uiso(min) Range 5.0 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference Cd1 -- O1A .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N17 -- C16_f .. 0.17 Ang.
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of Cd1 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 5.331 Check
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) . 1 Check

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Alert level G

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PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct. 2 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 5 Report
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) F1 -- B7 .. 9.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Cd1 -- O3A .. 5.9 s.u.
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PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage =          60 Note
PLAT367_ALERT_2_G Long?    C(sp?)-C(sp?) Bond  C13   -   C16     ..      1.53 Ang.
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in Structure ...      933 A**3
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........         3 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group    #         25 Check
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....         ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         5 Note
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed          ! Info
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=    0.600         7 Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ....... Please Check
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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
42 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
37 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

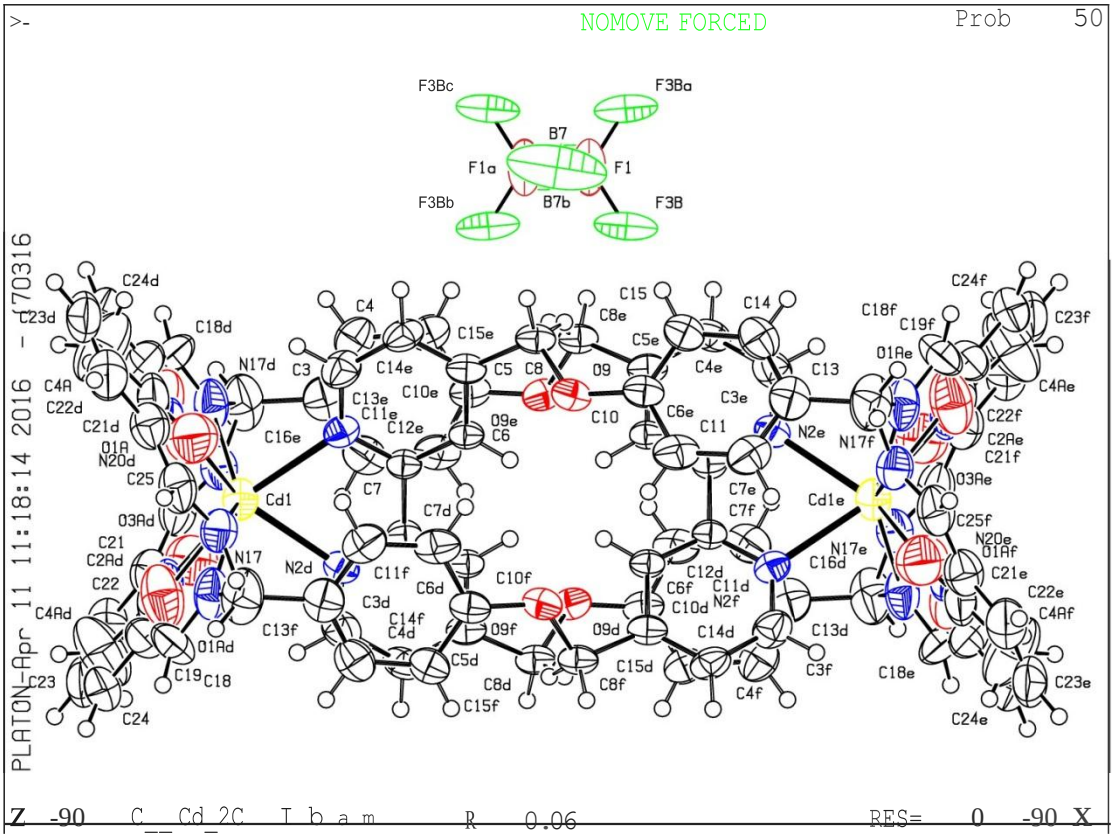
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock C_Cd_2C - ellipsoid plot



Cd-TK: $C_{105}H_{69}Cd_3F_9N_{15}O_{24}Re_3$, M = 2991.55, colourless needle, 0.180× 0.05 × 0.05 mm^3, , space group (No. 0), V = 15445.4(11) Å^3, Z = 6, D_c = 1.930 g/cm^3, F_{000} = 8676, Bruker apex2 duo, CuKα radiation, λ = 1.54178 Å, T = 100(2)K, $2\theta_{max}$ = 144.8º, 49542 reflections collected, 6716 unique (R_{int} = 0.0576). The structure was solved and refined using the programs SHELXT 2014/4 (Sheldrick, 2014) and SHELXL-2014 (Sheldrick, 2014) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and to prepare the figures. Final *GooF* = 1.081, *R1* = 0.0409, *wR2* = 0.1078, *R* indices based on 6371 reflections with I I > 2(I) (refinement on F^2), 479 parameters, 1 restraint. Lp and absorption corrections applied, μ = 12.429 mm^{-1}. Absolute structure parameter = 0.426(13) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

Detailed X-ray crystal structure determination for Cd-TK are available in Cambridge crystallography data center (CCDC), with deposition number of **CCDC 1443403.** All

crystallographic data are available free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C Users_MATTEO~1.LUS_Desktop_rombo_a

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No syntax errors found. CIF dictionary Interpreting this report

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	Calculated	Reported
Volume	15445.4(13)	15445.4(11)
Space group	R 3 c	R 3 c :h
Hall group	R 3 -2"c	R 3 -2"c
Moiety formula	C105 H69 Cd3 F9 N15 O12, 3(O4 Re)	?
Sum formula	C105 H69 Cd3 F9 N15 O24 Re3	C105 H69 Cd3 F9 N15 O24 Re3
Mr	2991.61	2991.55
Dx,g cm-3	1.930	1.930
Z	6	6
Mu (mm-1)	12.429	12.429
F000	8676.0	8676.0
F000'	8610.00	
h,k,lmax	22,22,63	21,22,63
Nref	6777[3394]	6716
Tmin,Tmax		0.516,0.754
Tmin'		

Correction method= # Reported T Limits: Tmin=0.516 Tmax=0.754 AbsCorr = MULTI-SCAN

Data completeness= 1.98/0.99 Theta(max)= 72.420

R(reflections)= 0.0409(6371) wR2(reflections)= 0.1131(6716)

S = 1.081 Npar= 479

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers ....          2 Check
 PLAT971_ALERT_2_B Check Calcd Residual Density  0.91A  From   O2C      2.89    eA-3
 PLAT971_ALERT_2_B Check Calcd Residual Density  1.09A  From   Re1B     2.82    eA-3
 PLAT971_ALERT_2_B Check Calcd Residual Density  0.95A  From   Re1D     2.73    eA-3
 PLAT971_ALERT_2_B Check Calcd Residual Density  1.07A  From   Re1C     2.65    eA-3
```

Alert level C

```
STRVA01_ALERT_4_C            Flack test results are ambiguous.
From the CIF: _refine_ls_abs_structure_Flack                0.426
From the CIF: _refine_ls_abs_structure_Flack_su               0.013
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...      Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...      Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...      Please Check
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ........        7.08 Note
PLAT244_ALERT_4_C Low     'Solvent' Ueq as Compared to Neighbors of      Re1B Check
PLAT244_ALERT_4_C Low     'Solvent' Ueq as Compared to Neighbors of      Re1C Check
PLAT244_ALERT_4_C Low     'Solvent' Ueq as Compared to Neighbors of      Re1D Check
PLAT342_ALERT_3_C Low Bond Precision on   C-C Bonds ..............    0.01619 Ang.
PLAT430_ALERT_2_C Short Inter D...A Contact   O2C    ..  O3D     ..       2.89 Ang.
 PLAT971_ALERT_2_C Check Calcd Residual Density  0.86A From   O3D      1.80    eA-3
 PLAT971_ALERT_2_C Check Calcd Residual Density  0.82A From   Cd1      1.55    eA-3
 PLAT972_ALERT_2_C Check Calcd Residual Density  0.37A From   Re1B    -1.63    eA-3
 PLAT972_ALERT_2_C Check Calcd Residual Density  0.24A From   Re1C    -1.54    eA-3
 PLAT973_ALERT_2_C Check Calcd Positive Residual Density on   Cd1      1.38    eA-3
 PLAT976_ALERT_2_C Check Calcd Residual Density  0.77A From   O2B     -0.54    eA-3
 PLAT976_ALERT_2_C Check Calcd Residual Density  0.71A From   O3D     -0.49    eA-3
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density          0 Note
```

Alert level G

```
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large  16.67 Why ?
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...          2 Units
PLAT242_ALERT_2_G  Low  'MainMol'  Ueq  as  Compared  to  Neighbors  of   C4A  Check
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          3 Note
```

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
5 **ALERT level B** = A potentially serious problem, consider carefully
18 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
15 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

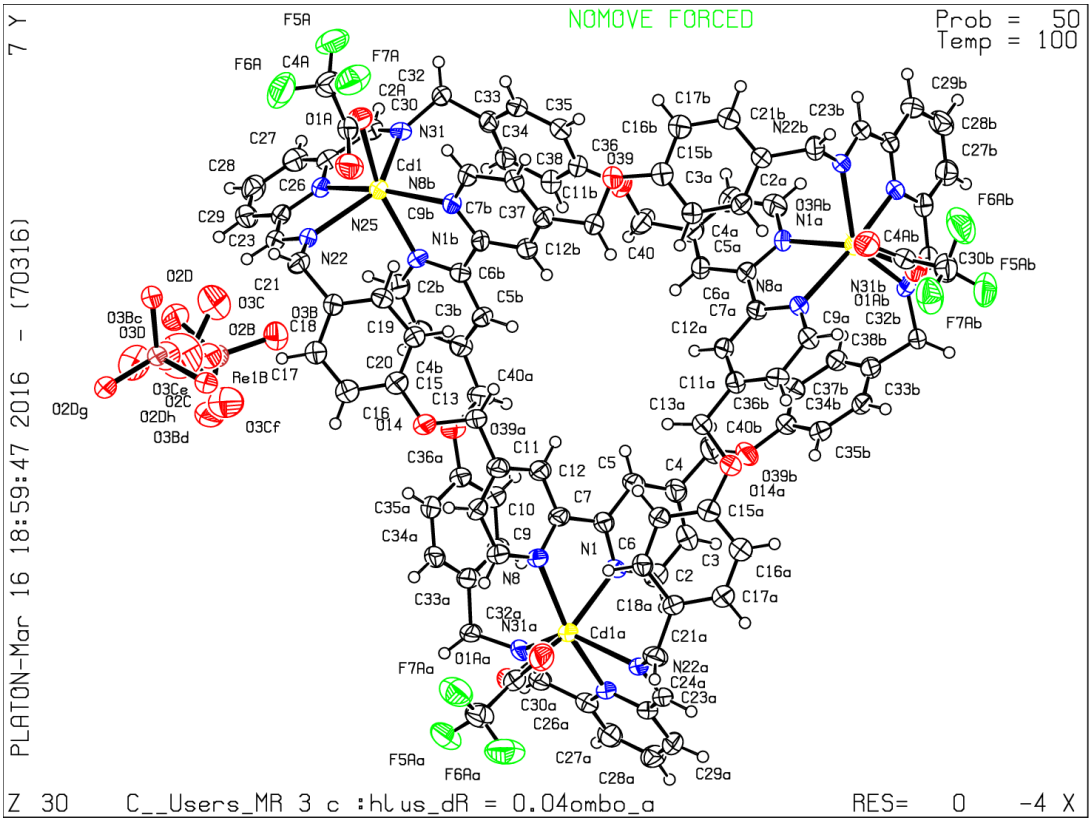
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.



PLATON version of 07/03/2016; check.def file version of 02/03/2016

Cd-SL: $C_{132}H_{108}Cd_4N_{20}O_{12}$, M = 2615.98, colourless prism, 0.164 × 0.122 × 0.084 mm^3, monoclinic, space group *C2/c* (No. 15), V = 20338(7) $Å^3$, Z = 4, D_c = 0.854 g/cm^3, F_{000} = 5312, Bruker D8 QUest, CuKα radiation, λ = 1.54178 Å, T = 100(2)K, $2\theta_{max}$ = 89.5º, 17110 reflections collected, 6612 unique (R_{int} = 0.1569). Final *GooF* = 1.370, *R1* = 0.2743, *wR2* = 0.4904, *R* indices based on 2273 reflections with I I > 2(I) (refinement on F^2), 253 parameters, 0 restraints. Lp and absorption corrections applied, μ = 3.639 mm^{-1}.

Detailed X-ray crystal structure determination for Cd-SL are available in Cambridge crystallography data center (CCDC), with deposition number of: **CCDC 1421588**. All crystallographic data are available free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C Cd-SK
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C Cd-SK

```
Bond precision:   C-C = 0.0613 A          Wavelength=1.54178

 Cell:          a=31.093(5)     b=34.507(6)          c=24.271(6)
                alpha=90        beta=128.646(4)      gamma=90
 Temperature:   100 K

                 Calculated                Reported
 Volume          20339(7)                  20338(7)
 Space group     C 2/c                     C 2/c
 Hall group      -C 2yc                    -C 2yc
 Moiety formula  C132 H108 Cd4 N20 O12     ?
 Sum formula     C132 H108 Cd4 N20 O12     C132 H108   Cd4 N20 O12
 Mr              2616.03                   2615.98
 Dx,g cm-3       0.854                     0.854
 Z               4                         4
 Mu (mm-1)       3.639                     3.639
```

F000	5312.0	5312.0
F000'	5328.02	
h,k,lmax	28,31,22	28,31,21
Nref	8111	6612
Tmin,Tmax	0.616,0.737	0.513,0.749
Tmin'	0.524	

Correction method= # Reported T Limits: Tmin=0.513 Tmax=0.749 AbsCorr = MULTI-SCAN

Data completeness= 0.815 Theta(max)= 44.729

R(reflections)= 0.2830(2273) wR2(reflections)= 0.5455(6612)

S = 1.447 Npar= 651

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

RFACG01_ALERT_3_A The value of the R factor is > 0.20
R factor given 0.283
RFACR01_ALERT_3_A The value of the weighted R factor is > 0.45
Weighted R factor given 0.545
THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4565
PLAT082_ALERT_2_A High R1 Value ..... 0.28 Report
PLAT084_ALERT_3_A High wR2 Value (i.e. > 0.25) ..... 0.55 Report
PLAT234_ALERT_4_A Large Hirshfeld Difference C56 -- C61 .. 0.32 Ang.
PLAT234_ALERT_4_A Large Hirshfeld Difference C59 -- C62 .. 0.32 Ang.
PLAT410_ALERT_2_A Short Intra H...H Contact H71 .. H73A .. 1.78 Ang.

Alert level B

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low .. 34 %
PLAT220_ALERT_2_B Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 10.0 Ratio
PLAT230_ALERT_2_B Hirshfeld Test Diff for C28 -- C29 .. 8.5 s.u.
PLAT234_ALERT_4_B Large Hirshfeld Difference N5 -- C4 .. 0.27 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference N5 -- C6 .. 0.26 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference N32 -- C33 .. 0.28 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference C3 -- C4 .. 0.28 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference C19 -- C22 .. 0.26 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference C42 -- C43 .. 0.30 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference C75 -- C76 .. 0.26 Ang.
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C4 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C7 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C29 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C33 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C43 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C50 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C61 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C62 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C70 Check

```
PLAT241_ALERT_2_B High     'MainMol' Ueq as Compared to Neighbors of       C73 Check
PLAT241_ALERT_2_B High     'MainMol' Ueq as Compared to Neighbors of       C76 Check
PLAT242_ALERT_2_B Low      'MainMol' Ueq as Compared to Neighbors of       N49 Check
PLAT242_ALERT_2_B Low      'MainMol' Ueq as Compared to Neighbors of         C2 Check
PLAT242_ALERT_2_B Low      'MainMol' Ueq as Compared to Neighbors of         C6 Check
PLAT242_ALERT_2_B Low      'MainMol' Ueq as Compared to Neighbors of       C28 Check
PLAT242_ALERT_2_B Low      'MainMol' Ueq as Compared to Neighbors of       C59 Check
PLAT242_ALERT_2_B Low      'MainMol' Ueq as Compared to Neighbors of       C65 Check
PLAT342_ALERT_3_B Low Bond Precision on  C-C Bonds ..............0.06129 Ang.
PLAT369_ALERT_2_B Long     C(sp2)-C(sp2) Bond  C24     -   C25    ..       1.58 Ang.
PLAT911_ALERT_3_B Missing # FCF Refl Between THmin & STh/L=    0.456       1489 Report
PLAT930_ALERT_2_B Check Twin Law ( 2 0 -1)[ 1 0    0] Estimated BASF       0.59
PLAT930_ALERT_2_B Check Twin Law ( 0 0    1)[ 1 0  2] Estimated BASF       0.64
PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers ....            3 Check
```

Alert level C

```
RINTA01_ALERT_3_C     The value of Rint is greater than 0.12
Rint given            0.157
PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full             ! Check
PLAT020_ALERT_3_C The value of Rint is greater than 0.12 .........        0.157 Report
PLAT222_ALERT_3_C Non-Solvent Resd 1     H Uiso(max)/Uiso(min) Range        9.3 Ratio
 PLAT230_ALERT_2_C Hirshfeld Test Diff for   N49    --   C50    ..       5.6     s.u.
 PLAT230_ALERT_2_C Hirshfeld Test Diff for   C2     --   C7     ..       5.3     s.u.
 PLAT230_ALERT_2_C Hirshfeld Test Diff for   C6     --   C7     ..       5.7     s.u.
 PLAT230_ALERT_2_C Hirshfeld Test Diff for   C29    --   C30    ..       6.5     s.u.
 PLAT230_ALERT_2_C Hirshfeld Test Diff for   C65    --   C70    ..       7.0     s.u.

PLAT230_ALERT_2_C Hirshfeld Test Diff for     C76    --  C77     ..        6.0 s.u.
PLAT234_ALERT_4_C Large Hirshfeld Difference Cd1     --  O1A     ..       0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference Cd1     --  N63     ..       0.25 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference Cd2     --  O2A     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference Cd2     --  N23     ..       0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference Cd2     --  N49     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O15     --  C14     ..       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O40     --  C37     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N9--    C8  ..      0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N26     --  C27     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N63     --  C62     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N72     --  C71     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N72     --  C73     ..       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C2--    C3  ..      0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C11     --  C12     ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C16     --  C21     ..       0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C25     --  C30     ..       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C27     --  C31     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C41     --  C42     ..       0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C51     --  C52     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C59     --  C60     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C64     --  C65     ..       0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C67     --  C71     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C69     --  C70     ..       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C73     --  C74     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C74     --  C75     ..       0.21 Ang.
PLAT241_ALERT_2_C High     'MainMol' Ueq as Compared to Neighbors of       O15 Check
PLAT241_ALERT_2_C High     'MainMol' Ueq as Compared to Neighbors of       C13 Check
PLAT241_ALERT_2_C High     'MainMol' Ueq as Compared to Neighbors of       C20 Check
PLAT241_ALERT_2_C High     'MainMol' Ueq as Compared to Neighbors of       C21 Check
PLAT241_ALERT_2_C High     'MainMol' Ueq as Compared to Neighbors of       C22 Check
PLAT241_ALERT_2_C High     'MainMol' Ueq as Compared to Neighbors of       C27 Check
```

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PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C35 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C51 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        Cd1 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        N26 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        N32 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C12 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C14 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C16 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C19 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C30 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C31 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C38 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C42 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C52 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C56 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C71 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C74 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C77 Check
PLAT363_ALERT_2_C Long     C(sp3)-C(sp2) Bond  C19    -   C22    ..       1.64 Ang.
PLAT363_ALERT_2_C Long     C(sp3)-C(sp2) Bond  C59    -   C62    ..       1.67 Ang.
PLAT369_ALERT_2_C Long     C(sp2)-C(sp2) Bond  C12    -   C13    ..       1.53 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact   H47    ..  H53     ..      1.97 Ang.
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     183.680 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     16.495 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     33.467 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     10.335 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     14.747 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......       6.116 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......       8.867 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......       3.971
CheckPLAT906_ALERT_3_C Large K value in the Analysis of Variance ......  6.010 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......  2.229 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......  4.131 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     3.044 Check
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          2 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         84 Report
PLAT072_ALERT_2_G SHELXL First   Parameter in WGHT  Unusually Large    0.20    Report
PLAT128_ALERT_4_G Alternate Setting for Input Space Group      C2/c    I2/a    Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          1 Report
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
PLAT650_ALERT_4_G SWAP Instruction Used to Model Solvent Disorder           ! Repor
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............     505     Note
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed           ! Info
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
PLAT908_ALERT_2_G Max. Perc. Data with I > 2*s(I) per Res.Shell .     66.71   %
PLAT931_ALERT_5_G Found Twin Law (        )[ 1 0  0] Estimated BASF    0.59    Check
PLAT931_ALERT_5_G Found Twin Law (        )[ 1 0  2] Estimated BASF    0.64    Check
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities .......     Please  Check
```

---

8 **ALERT level A** = Most likely a serious problem - resolve or explain
33 **ALERT level B** = A potentially serious problem, consider carefully
75 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
15 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

```
62 ALERT type 2 Indicator that the structure model may be wrong or deficient
24 ALERT type 3 Indicator that the structure quality may be low
41 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

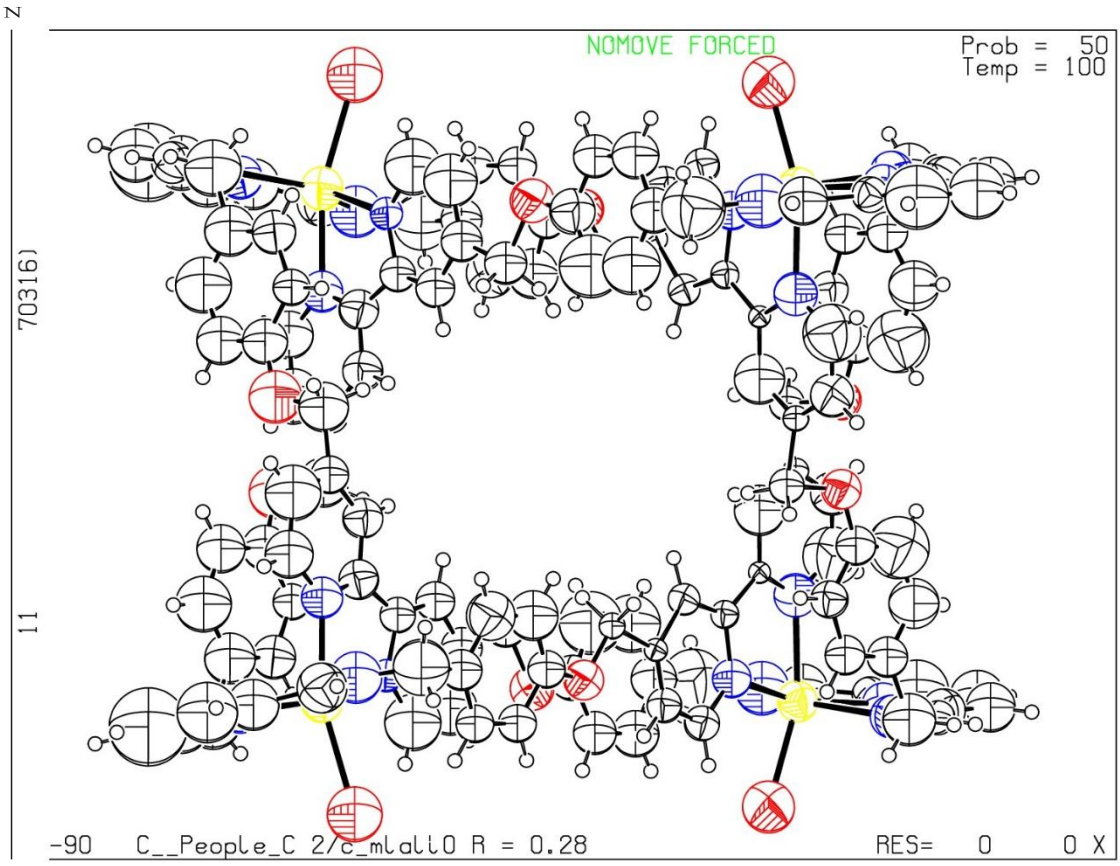
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock C_People_Thiru_MLALIO l_Copy - ellipsoid plot


NOMOVE FORCED
Prob = 50
Temp = 100
-90 C__People_C 2/c_mlall0 R = 0.28
RES= 0 0 X

10. DFT computational details and models for Cd- and Zn-links

Full geometry optimizations of M-[2]C, M-SL and M-TK (M = Zn or Cd) were performed employing DFT within the hybrid meta-GGA approximation with the M06[[5] functional and the Gaussian 09 package (Revision D.01).[6] In these calculations we used the standard 6-31G(d,p) basis set for C, H, N, O and Zn, while Cd was treated using a quasi-relativistic pseudopotential of the Stuttgart-Cologne family that includes 46 electrons in the core and describes the valence space using an uncontracted 4s4p basis set.[7] No symmetry constraints have been imposed during the optimizations. The default values for the integration grid (75 radial shells and 302 angular points) and the SCF energy convergence criteria (10^{-8}) were used in all calculations. Single point energy calculations in solution were performed using the polarizable continuum model (PCM); In particular, we used the integral equation formalism (IEFPCM) variant as implemented in Gaussian 09.[8]

The relative stability of the Zn(II) and Cd(II) knots was assessed by calculating the electronic energies for the following processes at the M06/6-31G(d,p) level:

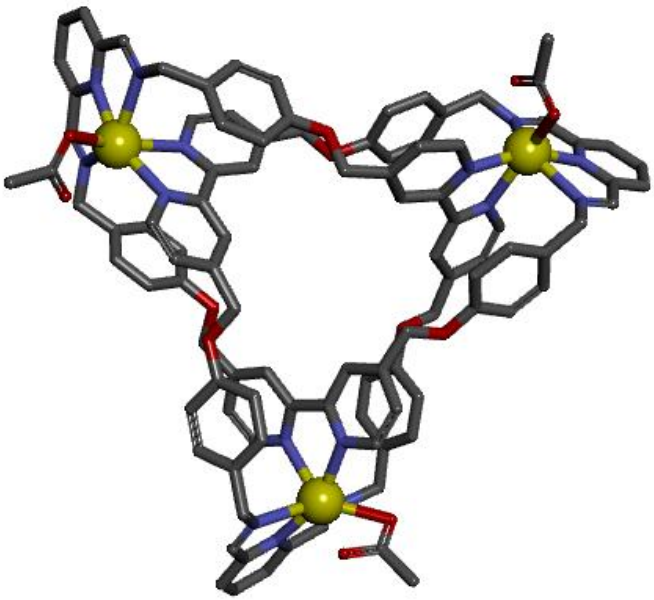
$$\text{Cd-[2]C} + 2\,[Zn(H_2O)_6]^{2+} \rightarrow \text{Zn-[2]C} + 2\,[Cd(H_2O)_6]^{2+} \qquad \Delta E = -70.0 \text{ kcal mol}^{-1}$$

$$\text{Cd-TK} + 3\,[Zn(H_2O)_6]^{2+} \rightarrow \text{Zn-TK} + 3\,[Cd(H_2O)_6]^{2+} \qquad \Delta E = -107.5 \text{ kcal mol}^{-1}$$

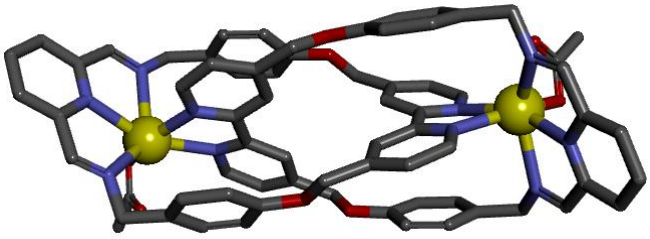
$$\text{Cd-SL} + 4\,[Zn(H_2O)_6]^{2+} \rightarrow \text{Zn-SL} + 4\,[Cd(H_2O)_6]^{2+} \Delta E = -139.2 \text{ kcal mol}^{-1}$$

The negative ΔE values obtained for all cases suggest that the Zn(II) knots are indeed more stable than the Cd(II) ones.

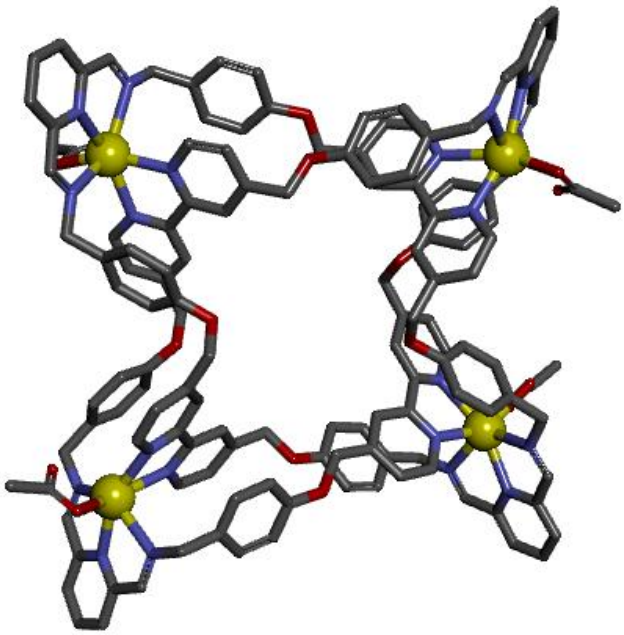
Cd-TK



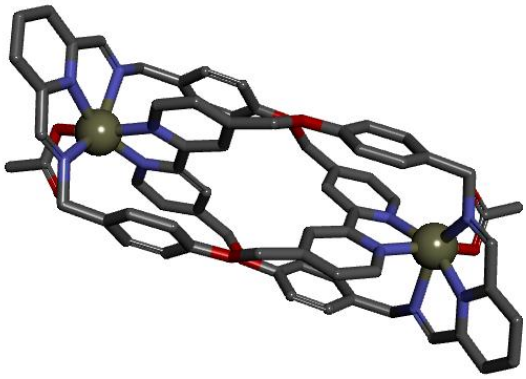
Cd-[2]C



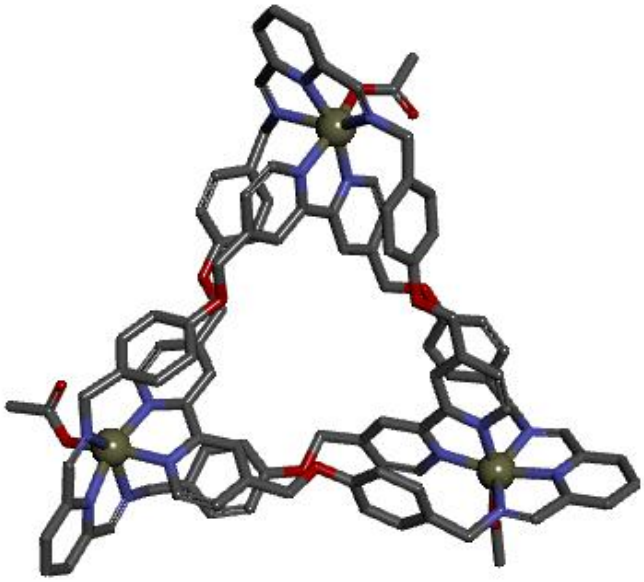
Cd-SL



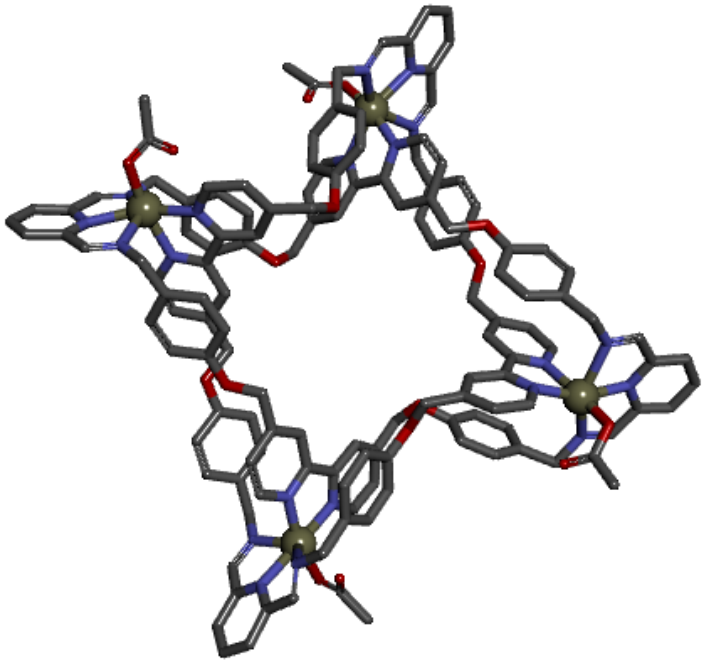
Zn-[2]C



Zn-TK



Zn-SL



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