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On the Supramolecular Properties of Neutral, Anionic and Cationic Cadmium Complexes Harvested from Dithiolate-Polyamine Binary Ligand Systems

Suman Adhikari[a*], Tirtha Bhattacharjee[b], Arijit Das[c], Subhadip Roy[d], Constantin Gabriel Daniliuc[e], Jan K. Zaręba[f], Antonio Bauzá[g], Antonio Frontera[g*]

[a] *Department of Chemistry, Govt. Degree College, Dharmanagar, Tripura (N)-799253, India*

[b] *Department of Chemistry, Bineswar Brahma Engineering College, Kokrajhar-783370, Assam, India*

[c] *Department of Chemistry, Bir Bikram Memorial College, Agartala, Tripura (W), India*

[d] *Department of Chemistry, The ICFAI University Tripura, Agartala-799210, Tripura, India*

[e] *Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, D-48149, Germany, Münster*

[f] *Advanced Materials Engineering and Modelling Group, Wrocław University of Science and Technology, Wybrzeze Wyspiańskiego 27, 50-370 Wrocław, Poland*

[g] *Department de Quimica, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Baleares), Spain*

***** Corresponding author address: Department of Chemistry, Govt. Degree College, Dharmanagar, Tripura (N)-799253, India (S. Adhikari). Departament de Quimica, Universitat de les Illes Balears, Crta. deValldemossa km 7.5, 07122 Palma de Mallorca (Baleares), Spain (A. Frontera).

E-mail addresses: sumanadhi@gmail.com (S. Adhikari); toni.frontera@uib.es (A. Frontera).

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***X-ray crystal structure collection and refinement details 1*:**

A yellow plate-like specimen of $C_8H_{12}CdN_2O_2S_4$, approximate dimensions 0.050 mm x 0.120 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1763 frames were collected. The total exposure time was 17.12 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 24854 reflections to a maximum θ angle of 66.85° (0.84 Å resolution), of which 1411 were independent (average redundancy 17.614, completeness = 99.2%, R_{int} = 5.75%, R_{sig} = 2.31%) and 1388 (98.37%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.1254(6) Å, b = 13.6595(6) Å, c = 8.5225(4) Å, volume = 1527.97(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 9933 reflections above 20 σ(I) with 12.24° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.857. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2060 and 0.4920. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pnma*, with Z = 4 for the formula unit, $C_8H_{12}CdN_2O_2S_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 137 variables converged at R1 = 3.26%, for the observed data and wR2 = 7.59% for all data. The goodness-of-fit was 1.244. The largest peak in the final difference electron density synthesis was 0.700 $e^-/Å^3$ and the largest hole was -0.741 $e^-/Å^3$ with an RMS deviation of 0.119 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.777 g/cm^3 and F(000), 808 e^-. CCDC number: 1990304.

X-ray crystal structure collection and refinement details of 2:

A colorless plate-like specimen of $C_{10}H_{22}CdN_6OS_2$, approximate dimensions 0.020 mm x 0.060 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1571 frames were collected. The total exposure time was 17.85 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 27384 reflections to a maximum θ angle of 66.76° (0.84 Å resolution), of which 2973 were independent (average redundancy 9.211, completeness = 99.7%, R_{int} = 4.39%, R_{sig} = 2.27%) and 2839 (95.49%) were

greater than $2\sigma(F^2)$. The final cell constants of a = 9.7864(5) Å, b = 10.9611(6) Å, c = 16.0220(8) Å, β = 102.095(2)°, volume = 1680.52(15) $Å^3$, are based upon the refinement of the XYZ-centroids of 9942 reflections above 20 σ(I) with 9.769° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.658. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2070 and 0.7840. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{10}H_{22}CdN_6OS_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 239 variables converged at R1 = 1.96%, for the observed data and wR2 = 4.58% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.416 $e^-/Å^3$ and the largest hole was -0.322 $e^-/Å^3$ with an RMS deviation of 0.067 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.655 g/cm^3 and F(000), 848 e^-. The hydrogen atoms at N3, N4, N5 and N6 were refined freely. The hydrogen atoms at O1 were refined freely, but with O-H distance restraints (DFIX and U-fixed value). CCDC number: 1990305.

X-ray crystal structure collection and refinement details of 3:

A yellow prism-like specimen of $C_{28}H_{52}Cd_3N_{18}S_6$, approximate dimensions 0.099 mm x 0.108 mm x 0.126 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 798 frames were collected. The total exposure time was 4.30 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 40692 reflections to a maximum θ angle of 72.44° (0.81 Å resolution), of which 8919 were independent (average redundancy 4.562, completeness = 99.8%, R_{int} = 7.46%, R_{sig} = 4.27%) and 8399 (94.17%) were greater than $2\sigma(F^2)$. The final cell constants of a = 14.6814(3) Å, b = 17.4409(4) Å, c = 17.6486(4) Å, volume = 4519.04(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9950 reflections above 20 σ(I) with 7.125° < 2θ < 144.7°. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2680 and 0.3350. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{28}H_{52}Cd_3N_{18}S_6$. The final anisotropic full-matrix least-squares refinement on F^2 with 629 variables converged at R1 = 3.13%, for the observed data and wR2 = 7.29% for all data. The goodness-of-fit was 1.064. The largest peak in the final

difference electron density synthesis was 1.048 $e^-/Å^3$ and the largest hole was -1.675 $e^-/Å^3$ with an RMS deviation of 0.107 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.720 g/cm^3 and F(000), 2344 e^-. Flack parameter was refined to -0.02(1). The hydrogen's at nitrogen atoms were refined freely, but partially with N-H distance restraints (DFIX and U-fixed value). CCDC number: 1990306.

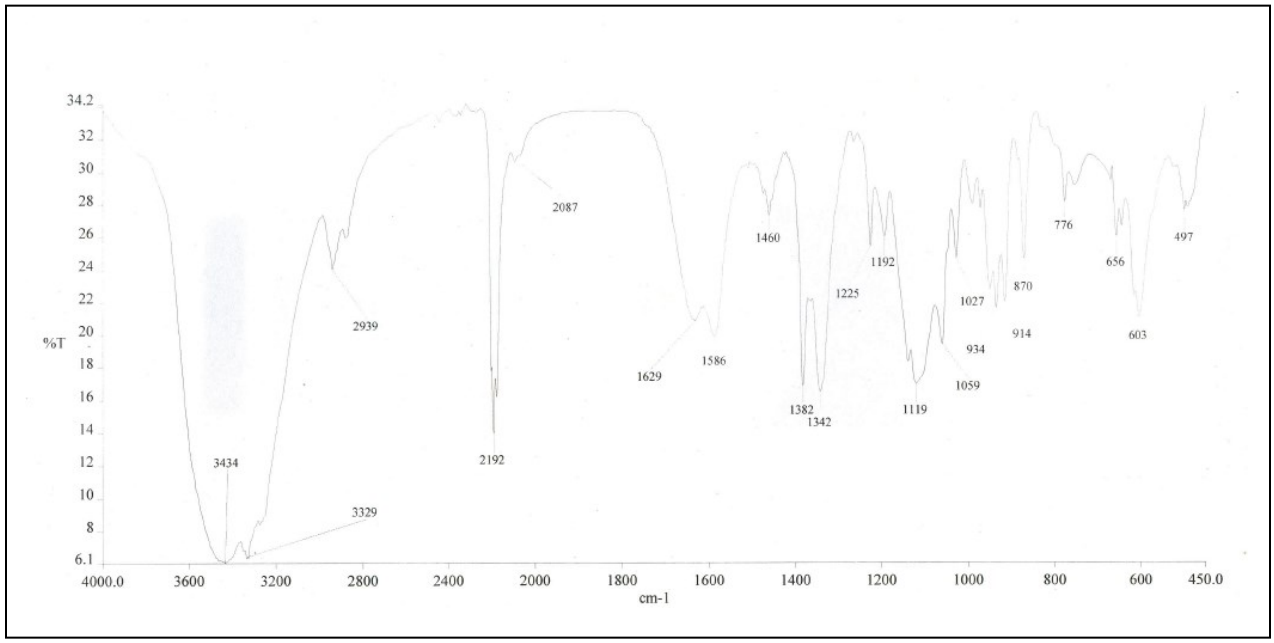

Figure S1.The FT-IR spectrum of complex **1**

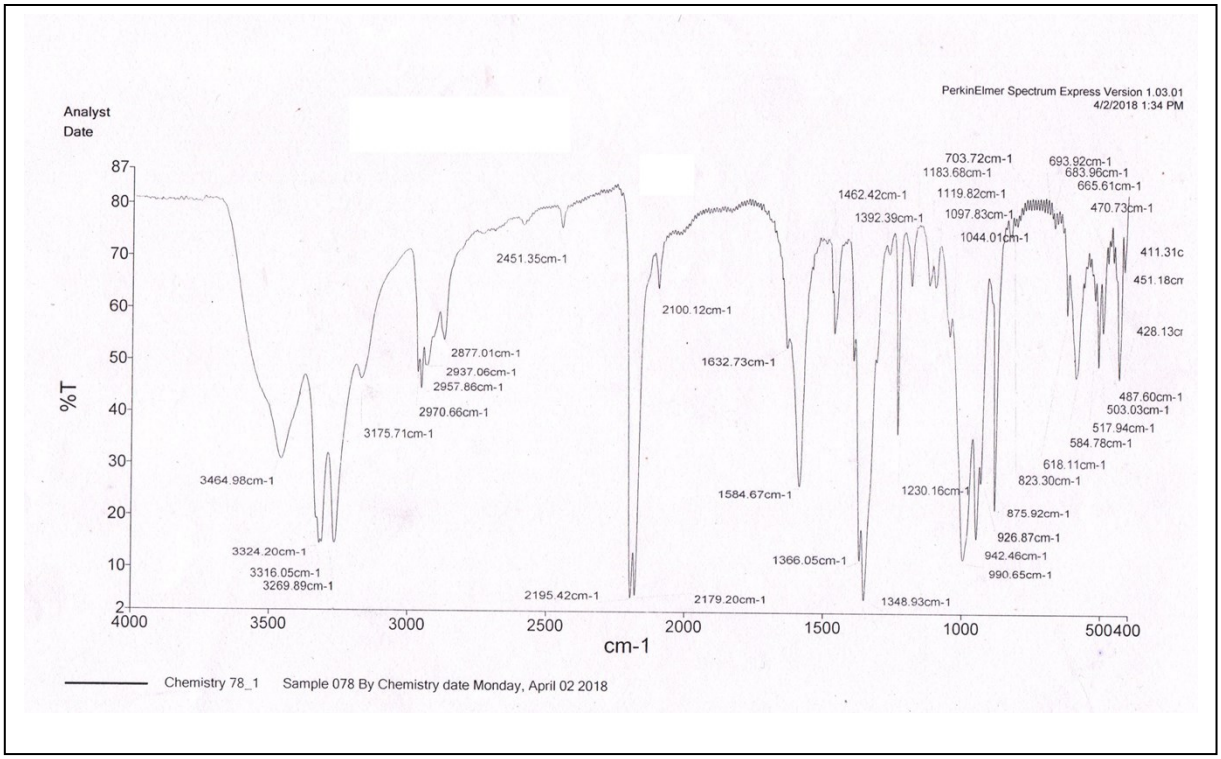

Figure S2.The FT-IR spectrum of complex **2**.

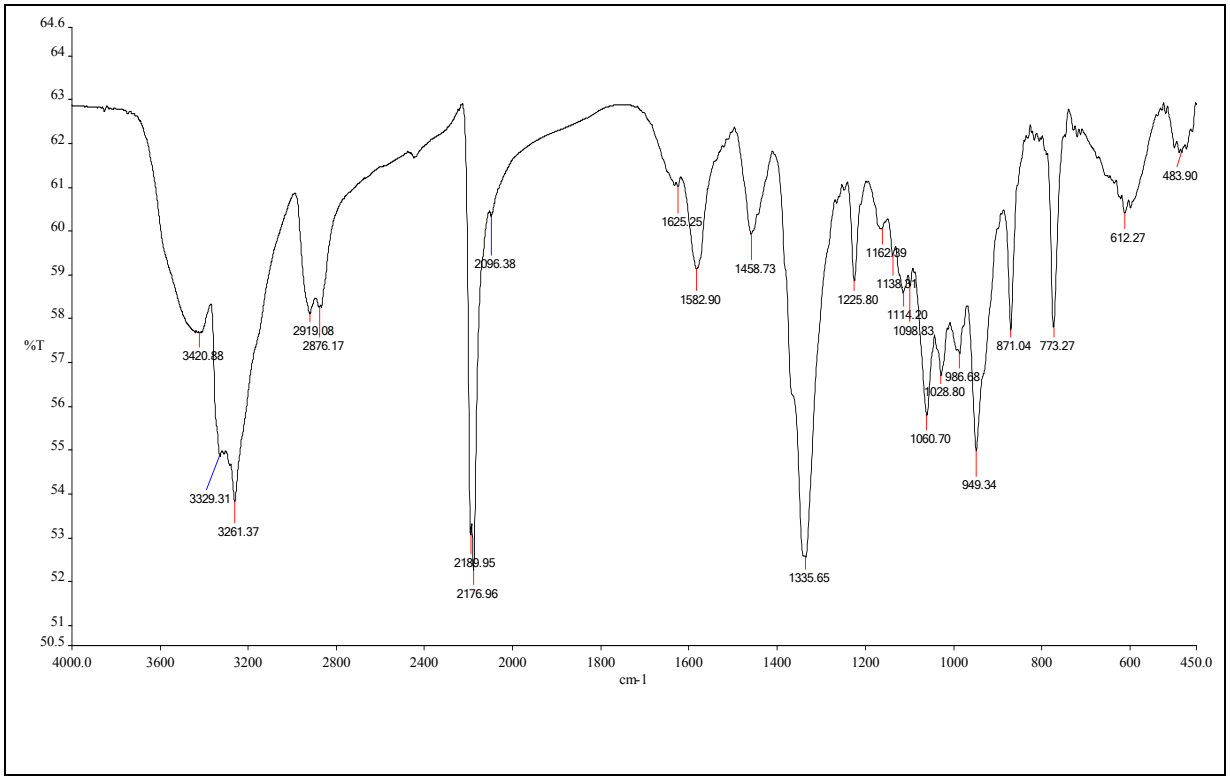

Figure S3.The FT-IR spectrum of complex **3**

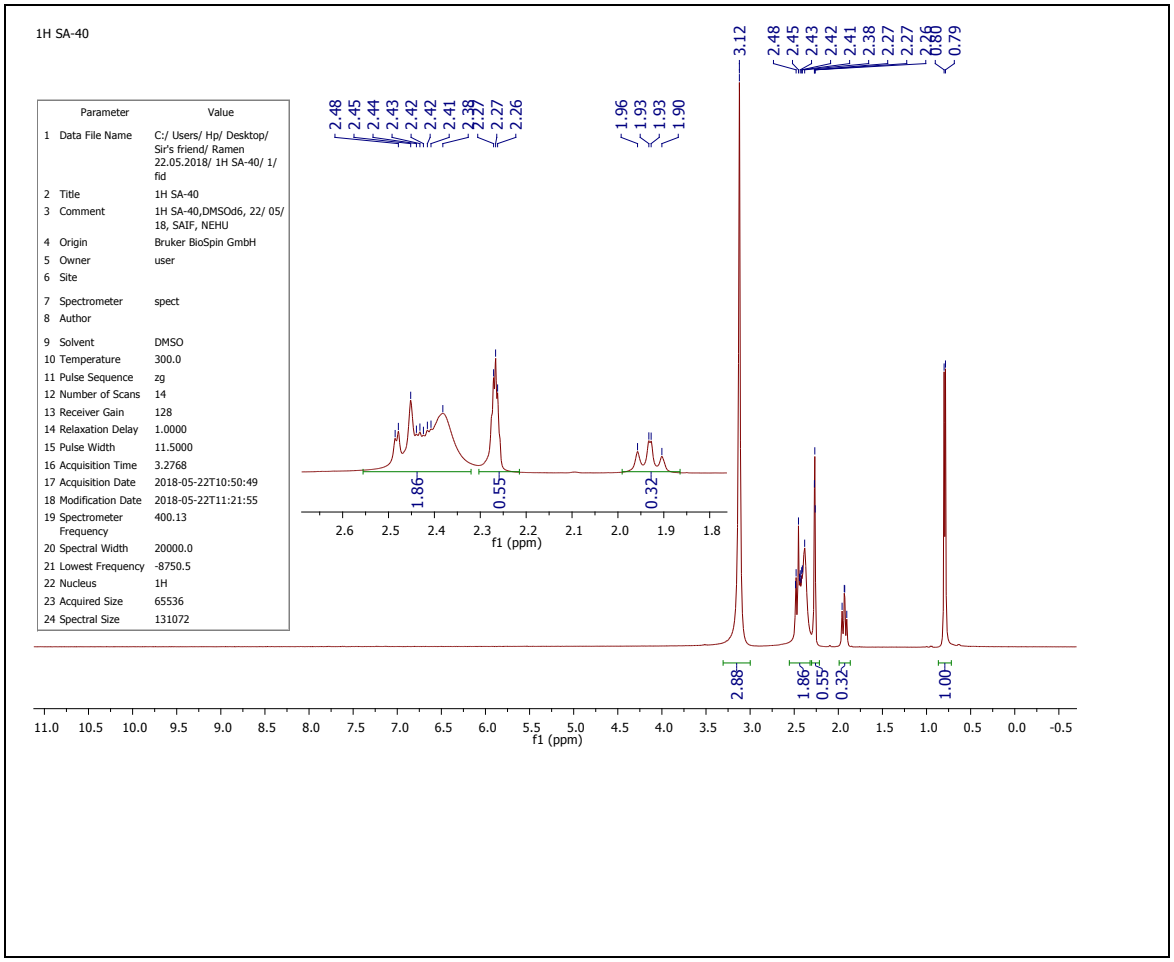

Figure S4. ^{1}H NMR spectrum of **2** in DMSO-d_6

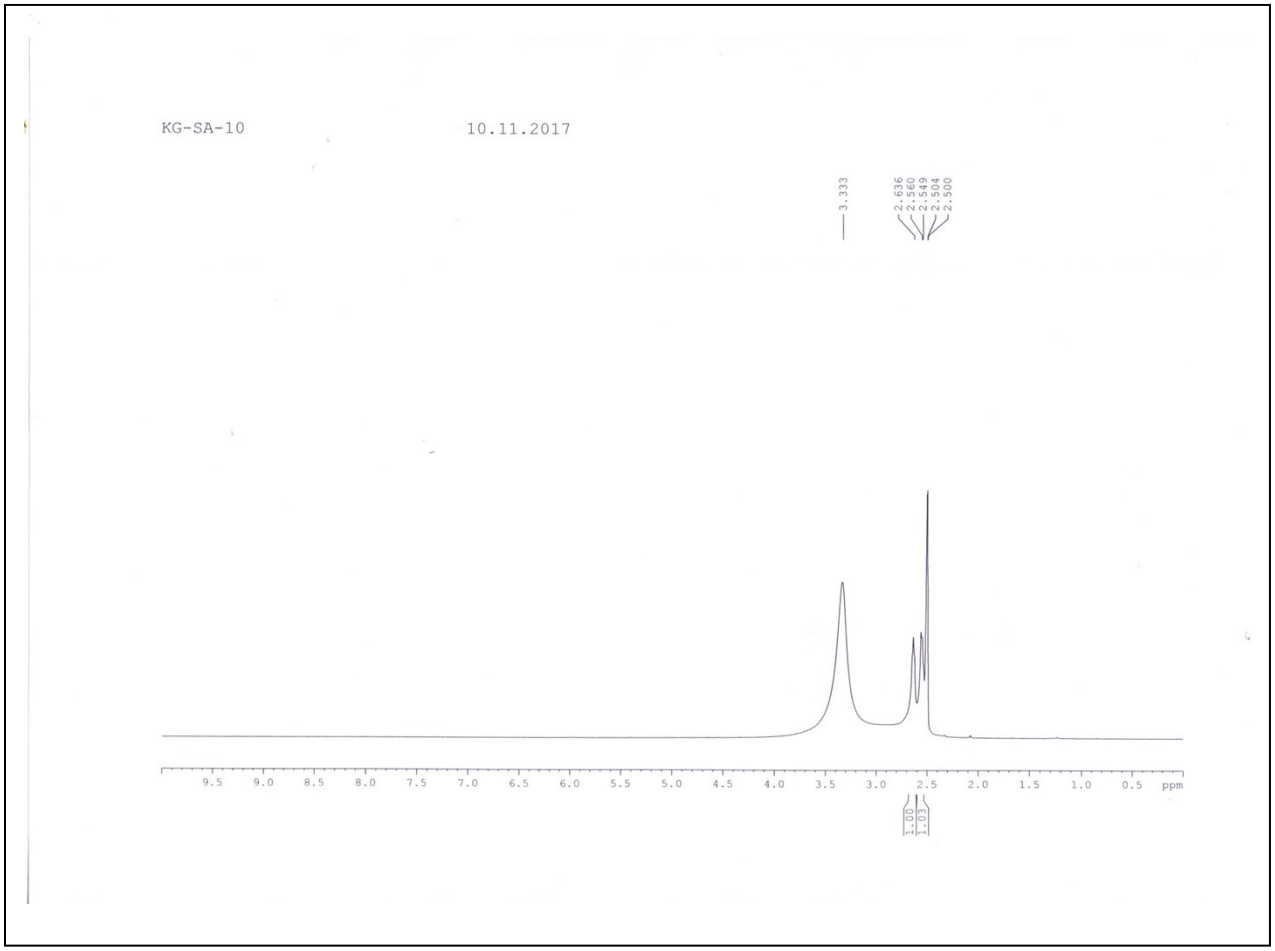

Figure S5. ^{1}H NMR spectrum of **3** in DMSO-d_6

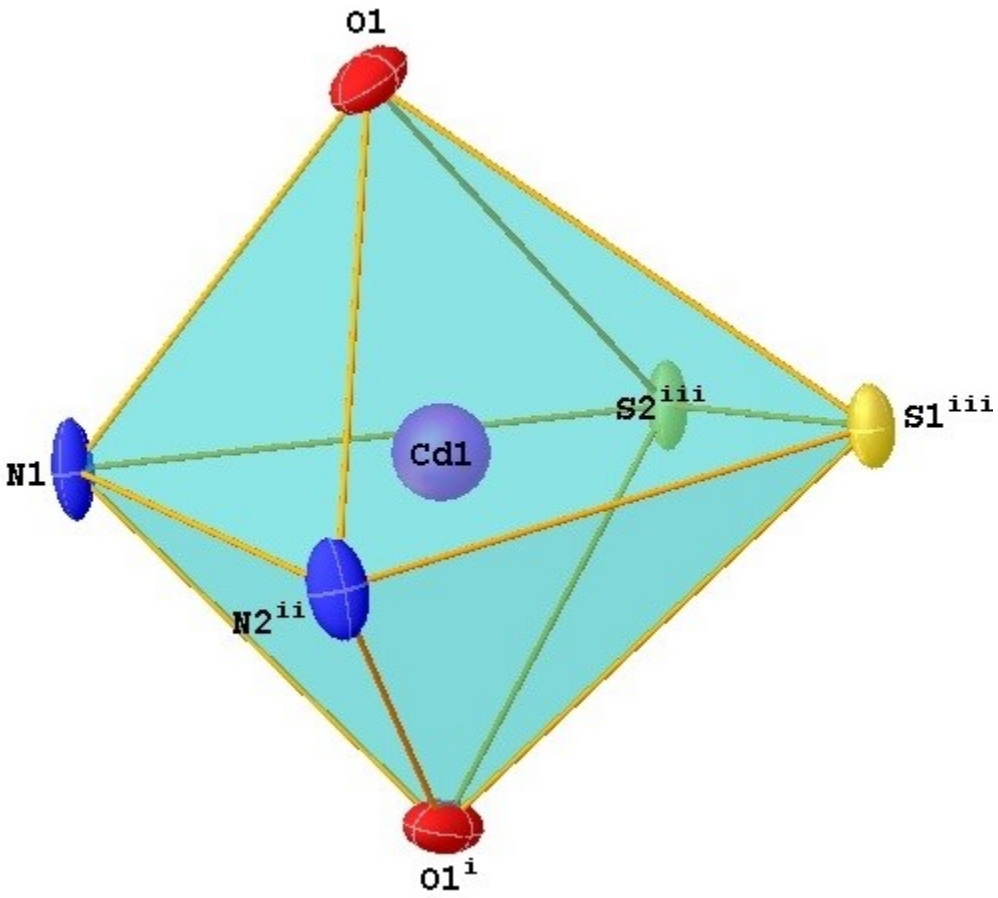

Figure S6. Coordination polyhedron of Cd(II) in *[Cd(i-mnt)(DMSO)$_2$]$_n$* (**1**)

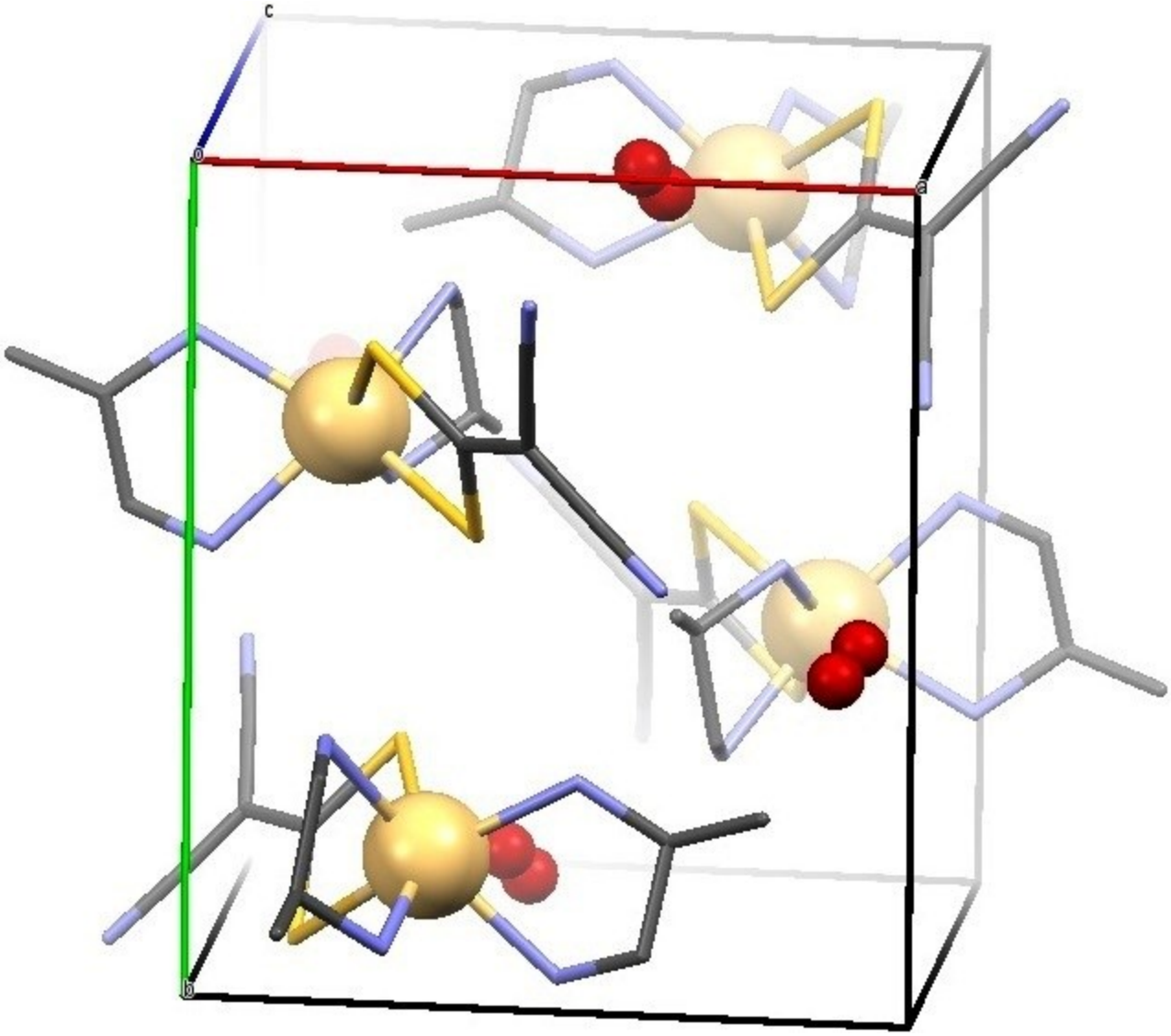

Figure S7. Polyhedral view of the unit cell packing for *{[Cd(i-mnt)pn]·2H$_2$O}* **(2)** comprising of four discrete molecules.

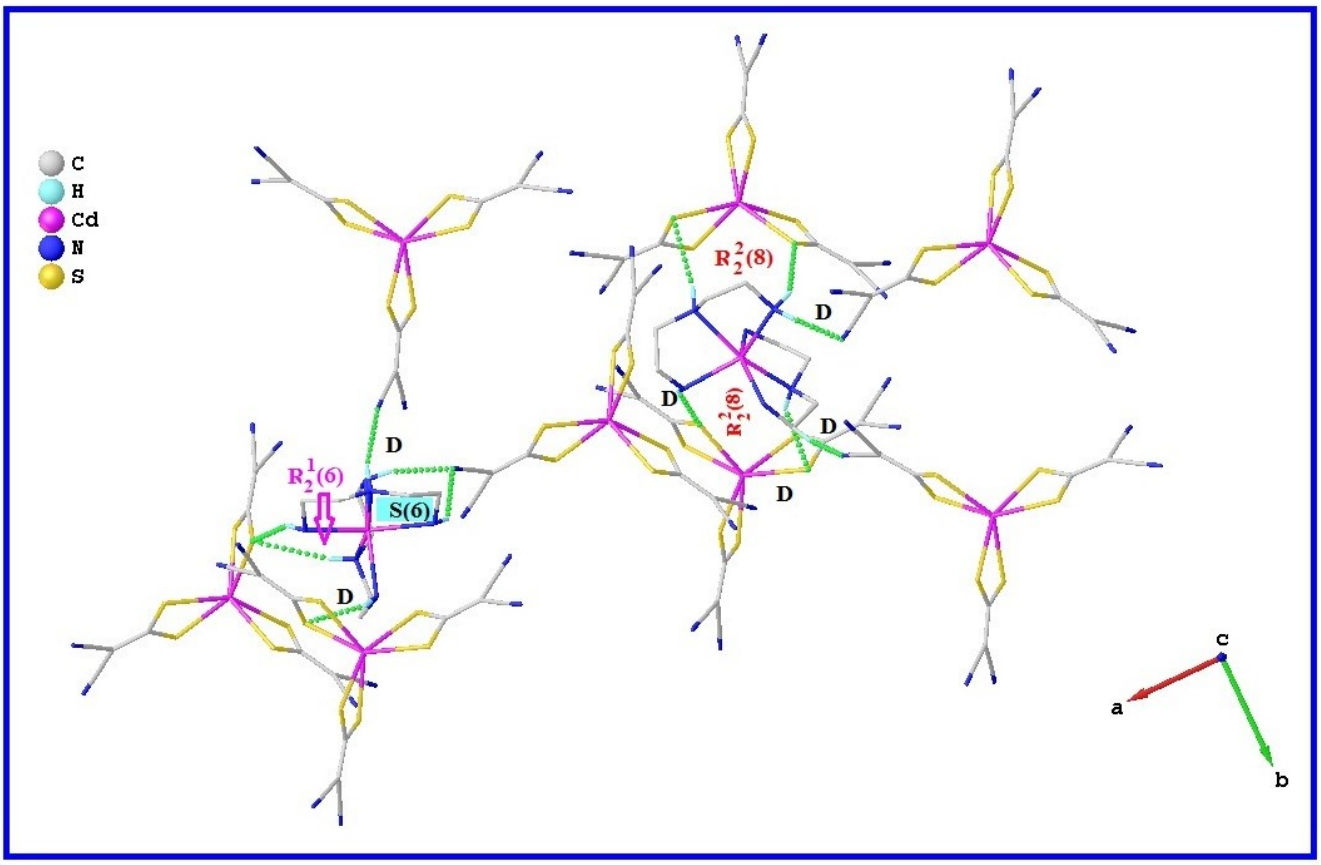

Figure S8. Graph-set motifs in *[Cd(i-mnt)$_3$][Cd(tren)$_2$]$_2$* **(3)** comprising of four discrete molecules.

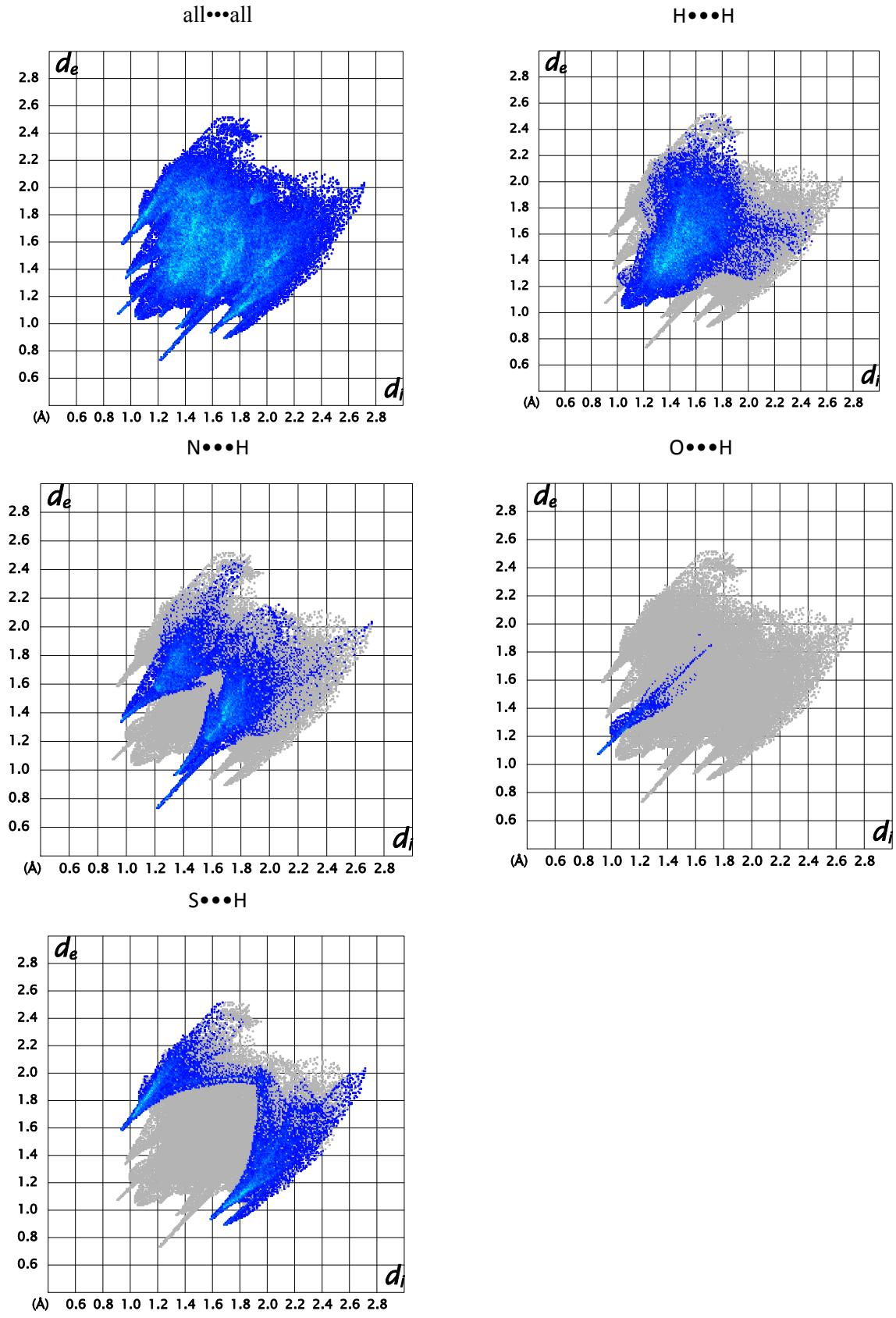

Figure S9. Decomposed fingerprint plots of complex molecule in **2**

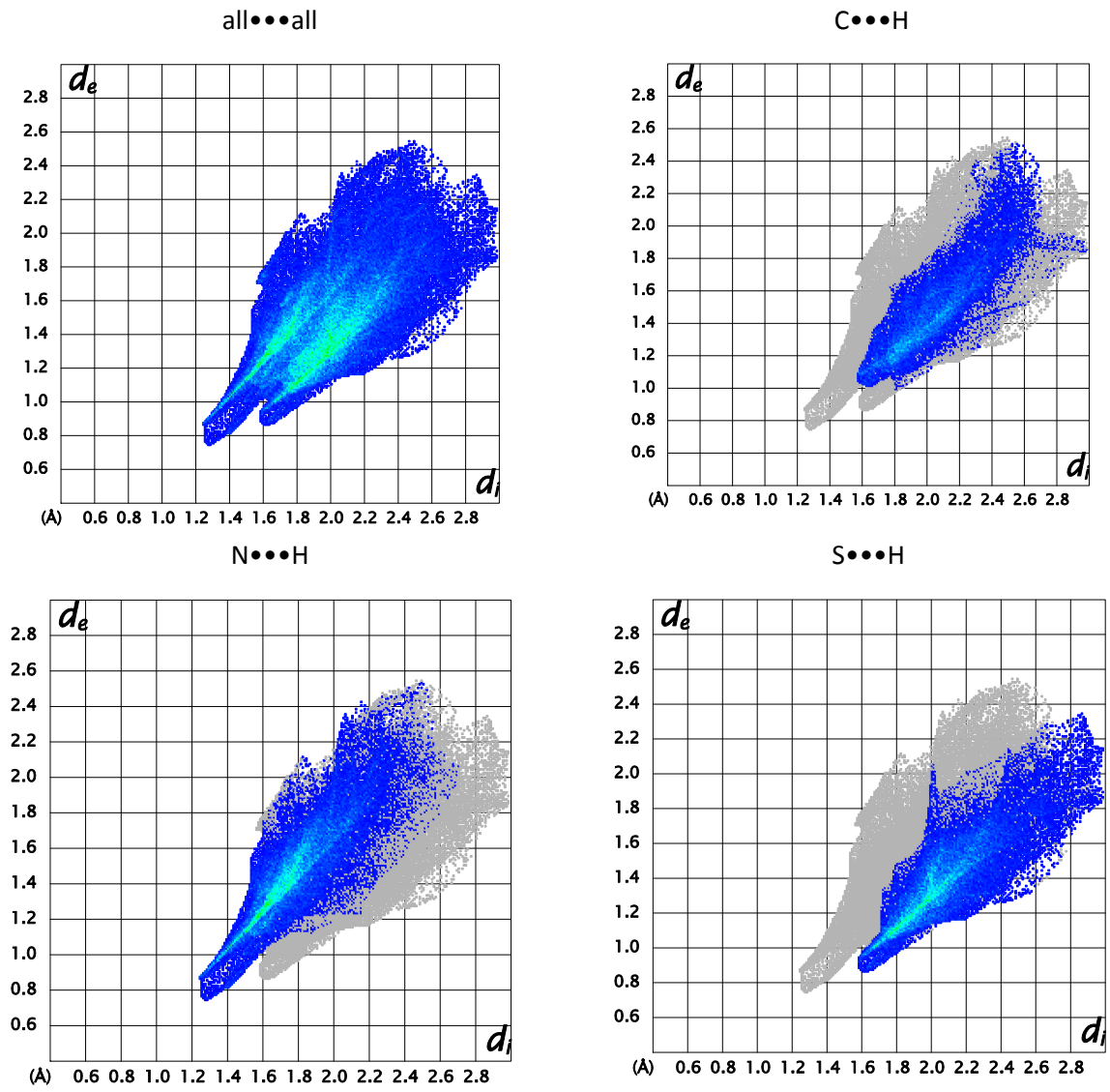

Figure S10. Decomposed fingerprint plots of **3A**

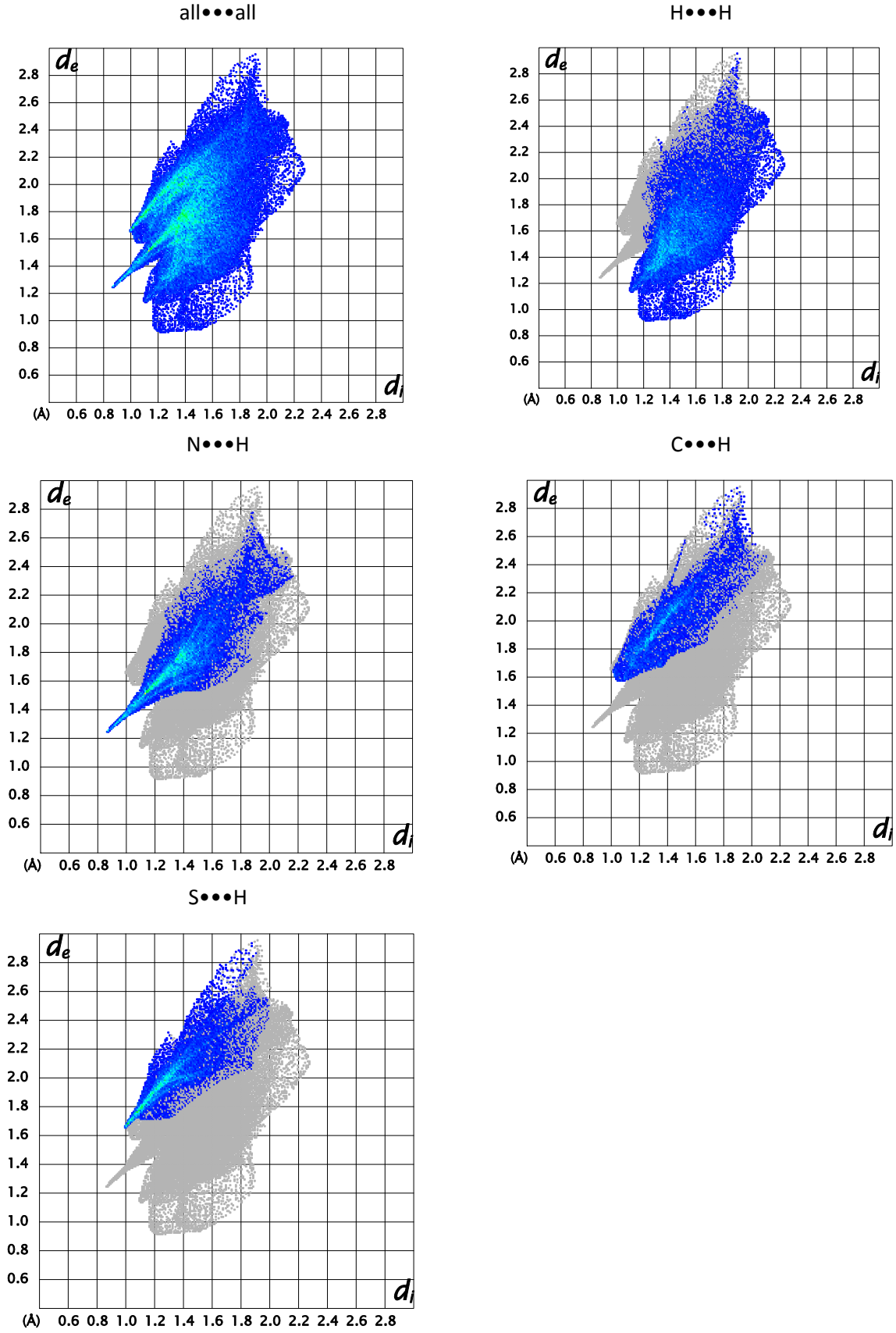

Figure S11. Decomposed fingerprint plots of **3B**

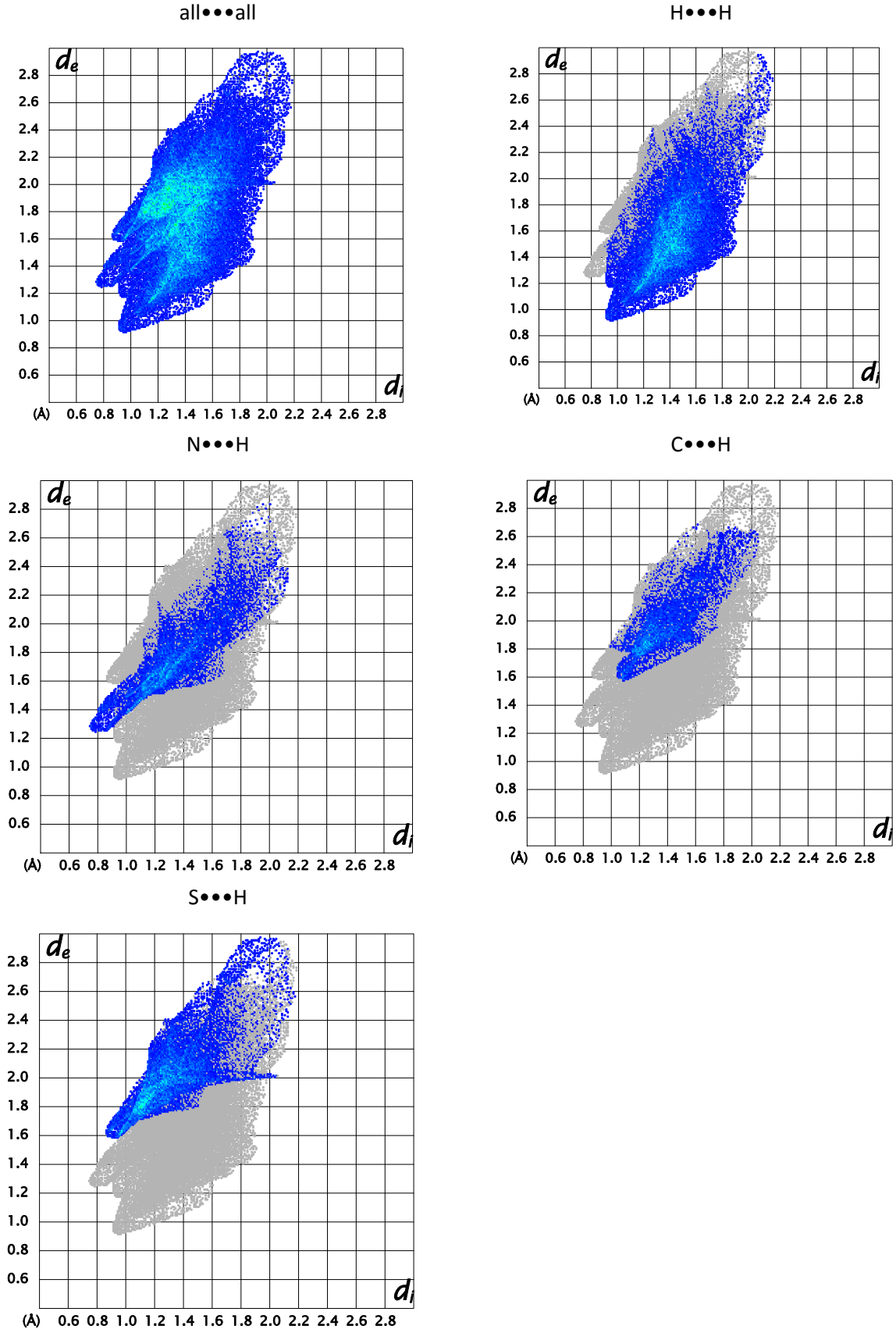

Figure S12. Decomposed fingerprint plots of **3C**

Table S1. Crystal data and structure refinement for 1-3.

	1	2	3
Empirical formula	$C_8H_{12}CdN_2O_2S_4$	$C_{10}H_{22}CdN_6OS_2$	$C_{28}H_{52}Cd_3N_{18}S_6$
Formula weight	408.84	418.85	1170.43
Temperature (K)	100(2)	152(2)	100(2)
Crystal system	Orthorhombic	monoclinic	orthorhombic
Space group	Pnma	$P2_1/n$	$P2_12_12_1$
a (Å)	13.1254(6)	9.7864(5)	14.6814(3)
b (Å)	13.6595(6)	10.9611(6)	17.4409(4)
c (Å)	8.5225(4)	16.0220(8)	17.6486(4)
α (°)	90	90	90
β (°)	90	102.095(2)	90
γ (°)	90	90	90
V (Å^3)	1527.97(12)	1680.52(15)	4519.04(17)
Z	4	4	4
D_{cal} (gcm^{-3})	1.777	1.655	1.720
μ (mm^{-1})	16.508	12.781	14.161
F(000)	808	848	2344
Crystal size (mm^3)	0.14 × 0.12 × 0.05	0.18 × 0.06 × 0.02	0.126 × 0.108 × 0.099
θ range for data collection (°)	6.12 to 66.85	4.88 to 66.76	3.56 to 72.44
Index ranges	$-15 \le h \le 14$, $-16 \le k \le 16$, $-10 \le l \le 10$	$-11 \le h \le 11$, $-13 \le k \le 12$, $-19 \le l \le 19$	$-18 \le h \le 18$, $-21 \le k \le 21$, $-21 \le l \le 21$
Reflections collected	24854	27384	40692

Independent reflections	1411 [R_{int} = 0.0575]	2973 [R_{int} = 0.0439]	8919 [R_{int} = 0.0746]
Absorption correction	Multi scan	Multi scan	Multi scan
Max and min transmission	0.49 and 0.42	0.78 and 0.52	0.34 and 0.27
Data/restraints/parameters	1411/144/163	2973/22/239	8919/169/629
Goodness-of-fit on F^2	1.256	1.035	1.064
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0325, wR_2 = 0.0756	R_1 = 0.0196, wR_2 = 0.0452	R_1 = 0.0313, wR_2 = 0.0711
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0758	R_1 = 0.0209, wR_2 = 0.0458	R_1 = 0.0347, wR_2 = 0.0729
Largest diff. in peak and hole (e $Å^{-3}$)	0.694 and -0.740	0.416 and -0.322	1.048 and -1.675

Table S2. Bond lengths (Å) for **1-3**

Complex 1					
N1—C3	1.141 (9)	S3—C5	1.781 (9)	C5^{i}—H5B^{i}	0.98
N1—Cd1	2.319 (5)	C5—H5A	0.98	C5^{i}—H5C^{i}	0.98
C3—C2	1.391 (9)	C5—H5B	0.98	C6^{i}—H6A^{i}	0.98
Cd1—N2^{ii}	2.348(10)	C5—H5C	0.98	C6^{i}—H6B^{i}	0.98
S1—C1	1.707 (8)	C6—H6A	0.98	C6^{i}—H6C^{i}	0.98
Cd1—O1	2.327 (5)	C6—H6B	0.98	C1—C2	1.425 (6)
Cd1—O1^{i}	2.327 (5)	C6—H6C	0.98	C1—S2	1.730 (6)
Cd1—S1^{iii}	2.665(12)	O1^{i}—S3^{i}	1.510 (5)	C2—C4	1.429 (6)
Cd1—S2^{iii}	2.603(19)	S3^{i}—C6^{i}	1.771 (10)	C4—N2	1.148 (5)
O1—S3	1.510 (5)	S3^{i}—C5^{i}	1.781 (9)		
S3—C6	1.771 (10)	C5^{i}—H5A^{i}	0.98		
Complex 2					
Cd1—N6	2.3685 (19)	C2—C4	1.416 (3)	Cd1—N3	2.3695 (19)
C2—C3	1.423 (3)	Cd1—N5	2.3709 (19)	C5—C6	1.524 (3)
Cd1—N4	2.3922 (18)	C5—H5A	0.99	Cd1—S1	2.6633 (5)
C5—H5B	0.99	Cd1—S2	2.7099 (5)	C6—C7	1.514 (3)
S1—C1	1.729 (2)	C6—H6	1.0	S2—C1	1.726 (2)
C7—H7A	0.98	N1—C3	1.148 (3)	C7—H7B	0.98
N2—C4	1.156 (3)	C7—H7C	0.98	N3—C5	1.469 (3)
C8—C9	1.519 (3)	N3—H3A	0.89 (3)	C8—H8A	0.99
N3—H3B	0.87 (3)	C8—H8B	0.99	N4—C6	1.479 (3)
C9—C10	1.519 (3)	N4—H4A	0.85 (3)	C9—H9	1.0
N4—H4B	0.85 (3)	C10—H10A	0.98	N5—C8	1.476 (3)
C10—H10B	0.98	N5—H5C	0.96 (3)	C10—H10C	0.98
N5—H5D	0.88 (3)	O1—H1A	0.880 (19)	N6—C9	1.476 (3)
O1—H1B	0.88 (2)	N6—H6A	0.81 (3)	O1A—H1C	0.89 (2)
N6—H6B	0.77 (4)	O1A—H1D	0.87 (2)	C1—C2	1.402 (3)

Complex 3					
C1—C2	1.407 (8)	C33—N34	1.470 (8)	N61—H61A	0.88 (2)
C1—S2	1.718 (6)	C33—H33A	0.99	N61—H61B	0.88 (2)
C1—S1	1.722 (7)	C33—H33B	0.99	C62—C63	1.503 (14)
Cd1—S6	2.5540 (17)	N34—C35	1.479 (9)	C62—H62A	0.99
Cd1—S4	2.5597 (16)	N34—H34	0.88 (3)	C62—H62B	0.99
Cd1—S1	2.6389 (15)	C35—C36	1.515 (10)	C63—N64	1.507 (12)
Cd1—S2	2.7212 (18)	C35—H35A	0.99	C63—H63A	0.99
Cd1—S5	2.9525 (17)	C35—H35B	0.99	C63—H63B	0.99
Cd1—S3	2.972 (2)	C36—N37	1.472 (8)	N64—C65	1.473 (13)
N1—C3	1.146 (10)	N47—H47A	0.87 (3)	N64—H64	0.89 (3)
C2—C4	1.415 (10)	N47—H47B	0.90 (3)	C65—C66	1.504 (15)
C2—C3	1.425 (10)	N51—C52	1.497 (11)	C65—H65A	0.99
Cd2—N34	2.365 (5)	N51—Cd3	2.457 (6)	C65—H65B	0.99
Cd2—N41	2.365 (5)	N51—H51A	0.90 (3)	C66—N67	1.481 (16)
Cd2—N31	2.367 (6)	N51—H51B	0.90 (3)	C66—H66A	0.99
Cd2—N47	2.380 (5)	C52—C53	1.490 (12)	C66—H66B	0.99
Cd2—N37	2.387 (6)	C52—H52A	0.99	N67—H67A	0.89 (3)
Cd2—N44	2.393 (6)	C52—H52B	0.99	N67—H67B	0.89 (3)
N2—C4	1.152 (11)	C53—N54	1.477 (10)	C36—H36A	0.99
N3—C13	1.139 (11)	C53—H53A	0.99	C36—H36B	0.99
S3—C11	1.710 (7)	C53—H53B	0.99	N37—H37A	0.89 (3)
N4—C14	1.169 (10)	N54—C55	1.466 (10)	N37—H37B	0.87 (3)
S4—C11	1.731 (7)	N54—Cd3	2.326 (6)	N41—C42	1.479 (9)
N5—C23	1.134 (9)	N54—H54	0.88 (3)	N41—H41A	0.89 (3)
S5—C21	1.719 (7)	C55—C56	1.493 (13)	N41—H41B	0.88 (3)
N6—C24	1.161 (9)	C55—H55A	0.99	C42—C43	1.528 (9)
S6—C21	1.726 (7)	C55—H55B	0.99	C42—H42A	0.99

C11—C12	1.393 (10)	C56—N57	1.473 (13)	C42—H42B	0.99
C12—C14	1.412 (11)	C56—H56A	0.99	C43—N44	1.467 (8)
C12—C13	1.434 (10)	C56—H56B	0.99	C43—H43A	0.99
C21—C22	1.412 (8)	N57—Cd3	2.375 (8)	C43—H43B	0.99
C22—C24	1.414 (9)	N57—H57A	0.89 (3)	N44—C45	1.472 (8)
C22—C23	1.430 (9)	N57—H57B	0.89 (3)	N44—H44	0.89 (3)
N31—C32	1.489 (9)	Cd3—N61A	2.306 (5)	C45—C46	1.513 (10)
N31—H31A	0.88 (3)	Cd3—N61	2.306 (5)	C45—H45A	0.99
N31—H31B	0.87 (3)	Cd3—N67A	2.368 (16)	C45—H45B	0.99
C32—C33	1.498 (10)	Cd3—N64	2.386 (7)	C46—N47	1.471 (9)
C32—H32A	0.99	Cd3—N67	2.388 (10)	C46—H46A	0.99
C32—H32B	0.99	N61—C62	1.466 (11)	C46—H46B	0.99

Symmetry codes: (i) x, 3/2-y, z; (ii) ½+x, y, 3/2-z; (iii) x, 3/2-y, 1+z

Table S3. Bond angles (^{0}) for **1-3**

Complex 1					
S1^{iii}—Cd1—S2^{iii}	68.9(2)	S3^{i}—C6^{i}—H6B^{i}	109.5(12)	S2^{iii}—Cd1—N1	106.6(3)
N1—Cd1—N2^{ii}	88.2(2)	N2^{ii}—Cd1—O1^{i}	98.9(4)	O1^{i}—Cd1—O1	168.6(7)
S1^{iii}—Cd1—N2^{ii}	96.3(17)	S1^{iii}—Cd1—O1	95.6(3)	Cd1—O1—S3	118.9(2)
S1^{iii}—Cd1—O1^{i}	95.6(3)	S2^{iii}—Cd1—O1	96.9(5)	O1—S3—C5	103.3(3)
S2^{iii}—Cd1—O1^{i}	84.9(5)	N1—Cd1—O1	84.3(3)	O1—S3—C6	106.0(5)
N1—Cd1—O1^{i}	84.3(3)	N2^{ii}—Cd1—O1	82.2(7)	S3—C5—H5A	109.4(3)
S3—C5—H5B	109.4(12)	S3^{i}—C6^{i}—H6C^{i}	109.5(15)	C1^{iii}—C2^{iii}—C4^{iii}	118.1(12)
S3—C5—H5C	109.5(15)	Cd1—S1^{iii}—C1^{iii}	84.0(10)	C3^{iii}—C2^{iii}—C4^{iii}	115.9(18)
S3—C6—H6A	109.5(7)	Cd1—S2^{iii}—C1^{iii}	85.6(3)	C2^{iii}—C3^{iii}—N1^{iii}	175.9(15)
S3—C6—H6B	109.5(9)	S1^{iii}—C1^{iii}—S2^{iii}	120.3(2)	C2^{iii}—C4^{iii}—N2^{iii}	172.7(4)
S3—C6—H6C	109.4(2)	S1^{iii}—C1^{iii}—C2^{iii}	120.1(11)	Cd1—N1—C3	169.6(5)
Cd1—O1^{i}—S3^{i}	118.9(2)	S2^{iii}—C1^{iii}—C2^{iii}	118.8(3)	N1—C3—C2	175.9(15)
O1^{i}—S3^{i}—C5^{i}	103.3(3)	C1^{iii}—C2^{iii}—C3^{iii}	124.9(3)	N2—C4—C2	172.7(4)
C3—C2—C4	115.9(18)	Cd1—N2^{ii}—C4^{ii}	152.4(15)	S3^{i}—C6^{i}—H6A^{i}	109.5(7)
C3—C2—C1	124.9(3)	S3^{i}—C5^{i}—H5B^{i}	109.5(12)	O1^{i}—S3^{i}—C6^{i}	106.0(5)
C4—C2—C1	118.1(12)	S3^{i}—C5^{i}—H5C^{i}	109.5(15)	S3^{i}—C5^{i}—H5A^{i}	109.5(3)
Complex 2					
N6—Cd1—N3	90.30 (7)	C1—C2—C4	121.72 (19)	N6—Cd1—N5	74.50 (7)
C1—C2—C3	122.2 (2)	N2—C4—C2	177.1 (2)	C6—C5—H5A	109.6
N3—Cd1—N5	156.46 (7)	N5—Cd1—N4	89.09 (7)	N5—Cd1—S1	94.68 (5)
C4—C2—C3	116.00 (19)	N3—C5—C6	110.34 (19)	N3—C5—H5B	109.6
N6—Cd1—N4	95.37 (8)	N6—Cd1—S1	160.93 (6)	N4—Cd1—S1	100.19 (5)
N1—C3—C2	177.4 (2)	N3—C5—H5A	109.6	C6—C5—H5B	109.6
N3—Cd1—N4	74.28 (7)	N3—Cd1—S1	104.44 (5)	N6—Cd1—S2	100.56 (6)
H5A—C5—H5B	108.1	N3—Cd1—S2	91.58 (5)	N4—C6—C7	113.50 (18)
N5—Cd1—S2	108.59 (5)	C7—C6—H6	107.9	Cd1—N3—H3A	113.2 (19)

N4—C6—C5	108.48 (18)	C1—S2—Cd1	85.35 (7)	H7A—C7—H7B	109.5
N4—Cd1—S2	158.76 (5)	C5—C6—H6	107.9	C5—N3—H3B	113.0 (19)
C7—C6—C5	111.1 (2)	C5—N3—Cd1	109.22 (13)	C6—C7—H7C	109.5
S1—Cd1—S2	67.532 (16)	C6—C7—H7A	109.5	Cd1—N3—H3B	103.8 (18)
N4—C6—H6	107.9	C5—N3—H3A	110.7 (19)	H7A—C7—H7C	109.5
C1—S1—Cd1	86.78 (7)	C6—C7—H7B	109.5	H3A—N3—H3B	107 (3)
H7B—C7—H7C	109.5	N5—C8—H8A	109.6	N5—C8—H8B	109.6
C6—N4—Cd1	109.36 (13)	Cd1—N4—H4A	109.2 (18)	Cd1—N4—H4B	111 (2)
N5—C8—C9	110.22 (18)	C9—C8—H8A	109.6	C9—C8—H8B	109.6
C6—N4—H4A	107.1 (18)	C6—N4—H4B	112 (2)	H4A—N4—H4B	109 (3)
H8A—C8—H8B	108.1	N6—C9—C8	109.29 (18)	N6—C9—C10	112.8 (2)
C8—N5—Cd1	107.88 (13)	C8—N5—H5C	108.7 (18)	Cd1—N5—H5C	114.0 (17)
C8—C9—C10	111.31 (19)	H5C—N5—H5D	107 (3)	C9—C10—H10B	109.5
C8—N5—H5D	112 (2)	C10—C9—H9	107.8	Cd1—N6—H6A	113 (2)
N6—C9—H9	107.8	C9—N6—Cd1	110.93 (14)	H10A—C10—H10B	109.5
Cd1—N5—H5D	107 (2)	C9—C10—H10A	109.5	C9—N6—H6B	109 (2)
C8—C9—H9	107.8	C9—N6—H6A	110 (2)	C9—C10—H10C	109.5
Cd1—N6—H6B	106 (2)	H10B—C10—H10C	109.5	C2—C1—S1	120.06 (16)
H10A—C10—H10C	109.5	C2—C1—S2	120.25 (16)	H1C—O1A—H1D	140 (10)
H6A—N6—H6B	108 (3)	H1A—O1—H1B	117 (5)	S2—C1—S1	119.68 (12)
Complex 3					
C2—C1—S2	120.5 (5)	S6—Cd1—S4	137.62 (6)	S6—Cd1—S1	105.58 (6)
C2—C1—S1	119.8 (5)	S4—Cd1—S2	112.38 (6)	S4—Cd1—S1	107.01 (5)
S2—C1—S1	119.6 (4)	S1—Cd1—S2	67.36 (5)	S6—Cd1—S2	104.75 (6)
S6—Cd1—S5	65.30 (5)	S1—Cd1—S3	86.58 (5)	C4—C2—C3	115.9 (6)
S4—Cd1—S5	94.71 (5)	S2—Cd1—S3	152.08 (5)	N34—Cd2—N41	96.34 (18)
S1—Cd1—S5	152.77 (5)	S5—Cd1—S3	118.16 (5)	N34—Cd2—N31	74.9 (2)
S2—Cd1—S5	89.50 (5)	C1—S1—Cd1	87.6 (2)	N41—Cd2—N31	103.0 (2)

S6—Cd1—S3	91.39 (6)	C1—C2—C4	123.3 (6)	N34—Cd2—N47	117.2 (2)
S4—Cd1—S3	64.52 (5)	C1—C2—C3	120.6 (6)	N41—Cd2—N47	145.6 (2)
N31—Cd2—N47	93.5 (2)	N47—Cd2—N44	74.2 (2)	C21—S6—Cd1	93.4 (2)
N34—Cd2—N37	74.97 (19)	N37—Cd2—N44	113.40 (19)	C12—C11—S3	121.7 (6)
N41—Cd2—N37	95.1 (2)	C1—S2—Cd1	85.1 (2)	C12—C11—S4	118.7 (5)
N31—Cd2—N37	146.3 (2)	N1—C3—C2	177.5 (8)	S3—C11—S4	119.6 (4)
N47—Cd2—N37	87.03 (19)	C11—S3—Cd1	81.4 (2)	C11—C12—C14	123.4 (7)
N34—Cd2—N44	166.99 (18)	N2—C4—C2	176.6 (9)	C11—C12—C13	121.3 (7)
N41—Cd2—N44	73.52 (18)	C11—S4—Cd1	94.5 (2)	C14—C12—C13	115.1 (7)
N31—Cd2—N44	99.0 (2)	C21—S5—Cd1	80.7 (2)	N3—C13—C12	178.2 (9)
N4—C14—C12	179.2 (8)	N6—C24—C22	177.4 (7)	N31—C32—H32A	109.6
C22—C21—S5	121.3 (5)	C32—N31—Cd2	108.9 (4)	C33—C32—H32A	109.6
C22—C21—S6	118.3 (5)	C32—N31—H31A	106 (5)	N31—C32—H32B	109.6
S5—C21—S6	120.4 (4)	Cd2—N31—H31A	115 (5)	C33—C32—H32B	109.6
C21—C22—C24	120.8 (6)	C32—N31—H31B	107 (7)	H32A—C32—H32B	108.2
C21—C22—C23	121.0 (6)	Cd2—N31—H31B	115 (7)	N34—C33—C32	109.4 (6)
C24—C22—C23	118.2 (5)	H31A—N31—H31B	104 (8)	N34—C33—H33A	109.8
N5—C23—C22	177.8 (6)	N31—C32—C33	110.1 (5)	C32—C33—H33A	109.8
N34—C33—H33B	109.8	N34—C35—H35B	109.7	C36—N37—H37B	113 (6)
C32—C33—H33B	109.8	C36—C35—H35B	109.7	Cd2—N37—H37B	111 (6)
H33A—C33—H33B	108.2	H35A—C35—H35B	108.2	H37A—N37—H37B	126 (8)
C33—N34—C35	115.5 (5)	N37—C36—C35	110.7 (5)	C42—N41—Cd2	112.4 (4)
C33—N34—Cd2	107.6 (4)	N37—C36—H36A	109.5	C42—N41—H41A	108 (6)
C35—N34—Cd2	108.3 (4)	C35—C36—H36A	109.5	Cd2—N41—H41A	114 (6)
C33—N34—H34	106 (5)	N37—C36—H36B	109.5	C42—N41—H41B	111 (6)
C35—N34—H34	112 (5)	C35—C36—H36B	109.5	Cd2—N41—H41B	100 (6)
Cd2—N34—H34	107 (5)	H36A—C36—H36B	108.1	H41A—N41—H41B	110 (9)
N34—C35—C36	109.7 (6)	C36—N37—Cd2	109.0 (4)	N41—C42—C43	111.0 (5)

N34—C35—H35A	109.7	C36—N37—H37A	95 (6)	N41—C42—H42A	109.4
C36—C35—H35A	109.7	Cd2—N37—H37A	100 (6)	C43—C42—H42A	109.4
N41—C42—H42B	109.4	Cd2—N44—H44	102 (7)	C46—N47—H47A	114 (6)
C43—C42—H42B	109.4	N44—C45—C46	108.5 (6)	Cd2—N47—H47A	99 (6)
H42A—C42—H42B	108.0	N44—C45—H45A	110.0	C46—N47—H47B	109 (5)
N44—C43—C42	108.7 (5)	C46—C45—H45A	110.0	Cd2—N47—H47B	113 (5)
N44—C43—H43A	110.0	N44—C45—H45B	110.0	H47A—N47—H47B	112 (8)
C42—C43—H43A	110.0	C46—C45—H45B	110.0	C52—N51—Cd3	105.4 (4)
N44—C43—H43B	110.0	H45A—C45—H45B	108.4	C52—N51—H51A	108 (7)
C42—C43—H43B	110.0	N47—C46—C45	111.3 (6)	Cd3—N51—H51A	107 (6)
H43A—C43—H43B	108.3	N47—C46—H46A	109.4	C52—N51—H51B	111 (7)
C43—N44—C45	113.6 (5)	C45—C46—H46A	109.4	Cd3—N51—H51B	114 (7)
C43—N44—Cd2	107.5 (4)	N47—C46—H46B	109.4	C53—C52—H52B	109.5
C45—N44—Cd2	109.4 (4)	C45—C46—H46B	109.4	N51—C52—H52B	109.5
C43—N44—H44	112 (7)	H46A—C46—H46B	108.0	H52A—C52—H52B	108.0
C45—N44—H44	111 (7)	C46—N47—Cd2	108.8 (4)	N54—C53—C52	108.2 (6)
N54—C53—H53A	110.1	C55—N54—H54	110 (5)	H55A—C55—H55B	108.2
C52—C53—H53A	110.1	C53—N54—H54	107 (5)	N57—C56—C55	111.0 (7)
N54—C53—H53B	110.1	Cd3—N54—H54	115 (5)	N57—C56—H56A	109.4
C52—C53—H53B	110.1	N54—C55—C56	109.9 (7)	C55—C56—H56A	109.4
H53A—C53—H53B	108.4	N54—C55—H55A	109.7	N57—C56—H56B	109.4
C55—N54—C53	115.4 (6)	C56—C55—H55A	109.7	C55—C56—H56B	109.4
C55—N54—Cd3	102.9 (4)	N54—C55—H55B	109.7	H56A—C56—H56B	108.0
C53—N54—Cd3	107.2 (4)	C56—C55—H55B	109.7	C56—N57—Cd3	109.8 (5)
C56—N57—H57A	104 (7)	N61—Cd3—N54	115.4 (2)	N57—Cd3—N64	88.7 (3)
Cd3—N57—H57A	125 (7)	N61—Cd3—N57	101.9 (3)	N61—Cd3—N67	142.4 (4)
C56—N57—H57B	104 (10)	N54—Cd3—N57	74.6 (3)	N54—Cd3—N67	100.6 (4)
Cd3—N57—H57B	124 (10)	N61—Cd3—N64	75.1 (3)	N57—Cd3—N67	97.7 (5)

H57A—N57—H57B	87 (10)	N54—Cd3—N64	161.6 (3)	N64—Cd3—N67	73.6 (4)
N61—Cd3—N51	90.3 (2)	Cd3—N61—H61A	105 (6)	N61—C62—H62B	110.3
N54—Cd3—N51	75.0 (2)	C62—N61—H61B	105 (6)	C63—C62—H62B	110.3
N57—Cd3—N51	149.6 (3)	Cd3—N61—H61B	111 (6)	H62A—C62—H62B	108.5
N64—Cd3—N51	121.5 (3)	H61A—N61—H61B	103 (9)	C62—C63—N64	110.7 (9)
N67—Cd3—N51	88.6 (5)	N61—C62—C63	107.3 (9)	C62—C63—H63A	109.5
C62—N61—Cd3	106.9 (6)	N61—C62—H62A	110.3	N64—C63—H63A	109.5
C62—N61—H61A	125 (6)	C63—C62—H62A	110.3	C62—C63—H63B	109.5
N64—C63—H63B	109.5	C65—N64—H64	99 (8)	C66—C65—H65A	110.2
H63A—C63—H63B	108.1	C63—N64—H64	107 (8)	N64—C65—H65B	110.2
C65—N64—C63	115.0 (9)	Cd3—N64—H64	126 (8)	C66—C65—H65B	110.2
C65—N64—Cd3	101.8 (6)	N64—C65—C66	107.7 (9)	H65A—C65—H65B	108.5
C63—N64—Cd3	107.9 (6)	N64—C65—H65A	110.2	N67—C66—C65	113.9 (9)
N67—C66—H66A	108.8	C65—C66—H66B	108.8	C66—N67—H67A	103 (10)
C65—C66—H66A	108.8	H66A—C66—H66B	107.7	Cd3—N67—H67A	121 (10)
N67—C66—H66B	108.8	C66—N67—Cd3	109.1 (8)	C66—N67—H67B	119 (10)
Cd3—N67—H67B	112 (10)	H67A—N67—H67B	93 (10)	C62A—N61A—Cd3	107.2 (10)

Symmetry codes: (i) x, 3/2-y, z; (ii) ½+x, y, 3/2-z; (iii) x, 3/2-y, 1+z

Table S4. Torsion angles (^{0}) for **1-3**

Complex 1			
Cd1—O1—S3—C6	−90.1 (5)	C3—C2—C4—C4i	94.2 (9)
Cd1—O1—S3—C5	167.0 (4)	C1—C2—C4—C4i	−94.4 (10)
Cd1—O1A—S3A—C6A	137.7 (12)	C3—C2—C4—N2i	85 (5)
Cd1—O1A—S3A—C5A	−118.0 (11)	C1—C2—C4—N2i	−104 (4)
C2—C1—S2—S2i	96.8 (6)	C4i—C2—C4—N2i	−9 (5)
S1—C1—S2—S2i	−96.9 (6)	C4i—C4—N2—N2i	−0.002 (8)
S1—C1—C2—C3	0.0000 (10)	N2i—C4—N2—C4i	0.002 (7)
S2—C1—C2—C3	166.2 (12)	C3—C2—C4A—C4Ai	99 (2)
S2i—C1—C2—C3	−166.2 (12)	C1—C2—C4A—C4Ai	−101 (3)
S2A—C1—C2—C3	180.0000 (10)	C3—C2—C4A—N2A	110 (50)
S1—C1—C2—C4	−171 (2)	C1—C2—C4A—N2A	−90 (50)
S2—C1—C2—C4	−4 (2)	C4Ai—C2—C4A—N2A	10 (50)
S2i—C1—C2—C4	23 (2)	C3—C2—C4A—N2Ai	100 (7)
S1—C1—C2—C4i	171 (2)	C1—C2—C4A—N2Ai	−100 (6)
S2—C1—C2—C4i	−23 (2)	C4Ai—C2—C4A—N2Ai	1 (8)
S2i—C1—C2—C4i	4 (2)	C4Ai—C4A—N2A—N2Ai	0.003 (4)
S1—C1—C2—C4A	−158 (5)	C2—C4A—N2A—N2Ai	−10 (50)
S2A—C1—C2—C4A	22 (5)	C2—C4A—N2A—C4Ai	−10 (50)
S1—C1—C2—C4Ai	158 (5)	N2Ai—C4A—N2A—C4Ai	−0.003 (4)
S2A—C1—C2—C4Ai	−22 (5)		
Complex 2			
Cd1—S2—C1—C2	171.31 (17)	Cd1—N4—C6—C7	−167.74 (16)
Cd1—S2—C1—S1	−7.80 (11)	Cd1—N4—C6—C5	−43.8 (2)
Cd1—S1—C1—C2	−171.18 (17)	N3—C5—C6—N4	61.1 (2)
Cd1—S1—C1—S2	7.92 (11)	N3—C5—C6—C7	−173.47 (18)
S2—C1—C2—C4	−4.7 (3)	Cd1—N5—C8—C9	−48.2 (2)

S1—C1—C2—C4	174.38 (17)	Cd1—N6—C9—C8	−38.4 (2)
S2—C1—C2—C3	177.72 (17)	Cd1—N6—C9—C10	−162.73 (16)
S1—C1—C2—C3	−3.2 (3)	N5—C8—C9—N6	59.4 (2)
Complex 3			
C2—C1—S1—Cd1	173.6 (5)	Cd2—N41—C42—C43	−30.0 (7)
S2—C1—S1—Cd1	−5.9 (3)	N41—C42—C43—N44	56.4 (7)
S2—C1—C2—C4	0.1 (10)	C42—C43—N44—C45	−173.7 (6)
S1—C1—C2—C4	−179.4 (5)	C42—C43—N44—Cd2	−52.5 (6)
S2—C1—C2—C3	176.0 (5)	C43—N44—C45—C46	164.8 (6)
S1—C1—C2—C3	−3.5 (9)	Cd2—N44—C45—C46	44.6 (6)
C2—C1—S2—Cd1	−173.7 (5)	N44—C45—C46—N47	−60.8 (8)
S1—C1—S2—Cd1	5.7 (3)	C45—C46—N47—Cd2	43.4 (6)
Cd1—S3—C11—C12	−179.4 (6)	Cd3—N51—C52—C53	39.0 (8)
Cd1—S3—C11—S4	−0.7 (3)	N51—C52—C53—N54	−65.7 (9)
Cd1—S4—C11—C12	179.5 (5)	C52—C53—N54—C55	168.8 (6)
Cd1—S4—C11—S3	0.8 (4)	C52—C53—N54—Cd3	54.8 (7)
S3—C11—C12—C14	176.5 (5)	C53—N54—C55—C56	−176.7 (6)
S4—C11—C12—C14	−2.3 (9)	Cd3—N54—C55—C56	−60.2 (6)
S3—C11—C12—C13	3.0 (9)	N54—C55—C56—N57	57.9 (8)
S4—C11—C12—C13	−175.8 (5)	C55—C56—N57—Cd3	−22.7 (8)
Cd1—S5—C21—C22	−174.8 (5)	Cd3—N61—C62—C63	57.2 (11)
Cd1—S5—C21—S6	4.2 (3)	N61—C62—C63—N64	−61.5 (14)
Cd1—S6—C21—C22	174.2 (5)	C62—C63—N64—C65	−80.4 (12)
Cd1—S6—C21—S5	−4.8 (4)	C62—C63—N64—Cd3	32.5 (12)
S5—C21—C22—C24	173.9 (5)	C63—N64—C65—C66	178.3 (9)
S6—C21—C22—C24	−5.1 (8)	Cd3—N64—C65—C66	61.9 (10)
S5—C21—C22—C23	−3.5 (9)	N64—C65—C66—N67	−55.8 (15)
S6—C21—C22—C23	177.4 (5)	C65—C66—N67—Cd3	17.2 (15)

Cd2—N31—C32—C33	−40.1 (6)	C32—C33—N34—Cd2	−49.1 (5)
N31—C32—C33—N34	61.8 (7)	C33—N34—C35—C36	167.5 (5)
C32—C33—N34—C35	−170.2 (5)	Cd2—N34—C35—C36	46.8 (6)
N34—C35—C36—N37	−60.4 (7)	C35—C36—N37—Cd2	40.3 (6)

Symmetry codes: (i) x, 3/2-y, z

Table S5. Hydrogen bond geometry for **1-3.**

D H....A	d (D H) (Å)	d (H....A) (Å)	d (D....A) (Å)	< (D H....A) (^{0})
complex 1				
C6 H6A....O1^{i}	0.98	2.35	3.273(13)	156.8
Complex 2				
N3-H3A....O1	0.89	2.43	3.094(13)	130.8
N3-H3A....O1A	0.89	2.30	2.963(12)	130.9
N3-H3B....S1^{i}	0.87	2.64	3.481(12)	160.6
N4-H4A....N2^{iii}	0.85	2.45	3.259(13)	158.7
N4-H4B....S2^{ii}	0.85	2.84	3.610(16)	152.4
N5-H5C....O1A^{ii}	0.96	2.03	2.978(14)	168.8
O1A-H1D....O1A^{vi}	0.87	2.37	3.219(11)	164.5
O1-H1B....S2^{iv}	0.87	2.69	3.552(14)	169.5
O1-H1A....N1^{v}	0.87	2.05	2.928(12)	172.1
Complex 3				
N41-H41B....N1	0.87	2.24	3.071(6)	159.0
N37-H37B....N1	0.87	2.42	3.118(5)	137.4
N34-H34....N5^{i}	0.89	2.33	3.169(5)	158.5
N44-H44....S3^{ii}	0.89	2.79	3.660(6)	165.7
N31-H31B....S3^{ii}	0.87	2.77	3.544(6)	148.9
N47-H47B....S5^{iii}	0.90	2.79	3.632(6)	156.4
N61-H61A....S6^{v}	0.88	2.65	3.425(7)	146.8
N54-H54....S1^{v}	0.88	2.68	3.459(6)	147.2
C52-H52A....N3^{vii}	0.99	2.47	3.425(6)	161.9
N67-H67B....N2^{vi}	0.89	2.26	3.150(4)	176.2
N67-H67A....S4^{iv}	0.89	2.61	3.393(5)	144.5
N64-H64....S2^{iv}	0.89	2.64	3.512(7)	167.3

Note: Symmetry codes for **1**: (i) $^{3}/_{2}$-x, 1-y, ½+z; for **2**: (i) ½-x, -½+y, ½-z; (ii) ½-x, ½+y, ½-z; (iii) -½+x, ½-y, ½+z; (iv) ½+x, ½-y, ½+z, (v) $^{3}/_{2}$-x, -½+y, ½-z; (vi) 1-x, -y, 1-z; for **3**: (i) 1-x, -½+y, $^{3}/_{2}$-z; (ii) 1+x, Y, z; (iii) $^{3}/_{2}$-x, 1-y, ½+z; (iv) -½+x, ½-y, 1-z; (v) ½-x, 1-y, -½+z; (vi) -1+x, y, z; (vii) -x, ½+y, $^{3}/_{2}$-z.

Table S6. Summary of Shape analysis for complexes **2** and **3**

Complex 2

HP-6	1	D6h	Hexagon		
PPY-6	2	C5v	Pentagonal pyramid		
OC-6	3	Oh	Octahedron		
TPR-6	4	D3h	Trigonal prism		
JPPY-6	5	C5v	Johnson pentagonal pyramid J2		
Structure [ML6]	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
Cd1	32.066	20.789	4.273	8.578	24.022

Complex 3

P-6	1	D6h	Hexagon		
PPY-6	2	C5v	Pentagonal pyramid		
OC-6	3	Oh	Octahedron		
TPR-6	4	D3h	Trigonal prism		
JPPY-6	5	C5v	Johnson pentagonal pyramid J2		
Structure [ML6]	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
Cd1	32.142	14.525	9.004	7.255	17.426
Cd2	33.408	14.364	6.921	6.834	18.021
Cd3	33.477	16.586	6.355	6.352	20.554