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Supplemental Information for:

Azide-Bridged Cd(II) 1D Coordination Polymer with Cd_{13} Nano-Crown-like Cluster

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1. Experimental Section

Materials and physical measurements: *All metal-azides are potentially explosive. Only micro-scaled reactions may be performed, and all operations must be handled with necessary precautionary measures*. All the starting chemicals were of A. R. grade and used as received. Elemental analyses (C, H, N) were performed on an Elementar Vario EL analyser. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer (KBr Pellet). Thermogravimetric analysis was performed on *TA* Instruments Q500 equipment from room temperature to 800 °C under air or N_2 flow at a heating rate of 10 °C/min. Powder X-ray diffraction data was collected on a SIEMENS D5005 X-Ray Diffractometer with Cu-Ka radiation (λ = 1.5406 Å). Photoluminescence was measured using a Perkin Elmer LS55 Luminescence Spectrometer.

Synthesis of $[Cd_{15}(2\text{-Acpy})_{12}(N_3)_{30}]_n(CH_3OH)_n$ (1). A mixture of 2-acetylpyridine (41 mg, 0.33 mmol) and $Cd(ClO_4)_2{\cdot}6H_2O$ (210 mg, 0.5 mmol) was stirred in CH_3OH solution (4 mL) for two minutes, then a CH_3OH solution (8 mL) of NaN_3 (65 mg, 1 mmol) was added into the above mixture under stirring. After stirring for about five minutes at room temperature, the resulting mixture was filtered. The filtrate was allowed to stand and evaporate at room temperature, and it afforded weak yellow crystals of **1** within two days. Yield: 45 mg, 31 % (according to Cd). Anal. Calcd. For $C_{85}H_{88}Cd_{15}N_{102}O_{13}$ (4432.58): C, 23.03; H, 2.00; N, 32.23 %. Found: C, 22.82; H, 2.12; N, 31.92 %. Main IR (cm^{-1}): 2084 and 2035bvs (ν_{as}-N_3), 1672s (ν_{as}-C=O), 1629m, 1592m, 1439m, 1357m, 1334m, 1306m (ν_s-N_3), 1285m, 1247s, 1161m, 1095m, 1014m, 784m and 613m (δ-N_3).

2. X-ray crystallography

All measurements were conducted on a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo Kα radiation of λ = 0.71073 Å (Table 1). Empirical absorption corrections were applied using the Sortav program.[1] The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELX program.[2] For the disordered ligand 2-acetylpyridine in complex **1**, no hydrogen atom was placed on it and the non-hydrogen atoms were refined isotropically. CCDC reference number 900349 (**1**).

References:

1. (*a*) R. H. Blessing, *Acta Crystallogr.*, *Sect. A*, 1995, **51**, 33–38; (*b*) R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421–426.

2. (*a*) G. M. Sheldrick, *SHELXTL Version 5.1*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1998; (*b*) G. M. Sheldrick, *SHELXL-97*, *PC Version*, University of Göttingen, Germany, 1997.

3. Table S1 Crystallographic data for complex **1**.

Formula	$C_{85}H_{88}Cd_{15}N_{102}O_{13}$
M_w	4432.58
Crystal system	Monoclinic
Space group	$P\ 2_1/n$
a / Å	15.4565(2)
b / Å	28.6559(3)
c / Å	16.8825(2)
β / °	91.2664(6)
V / Å^3	7475.8(2)
Z	2
D_{calc} / g cm^{-3}	1.969
μ / mm^{-1}	2.171
T / K	293(2)
θ range / °	3.46–27.49
Reflections collected	77942
Independent reflections [R_{int}]	17034 [0.0861]
Parameters	966
GOF	0.890
R_1 ($I > 2\sigma(I)$)	0.0370
wR_2 (all data)	0.0773

4. Table S2 Selected bond lengths (Å) and angles (°) for complex **1**.

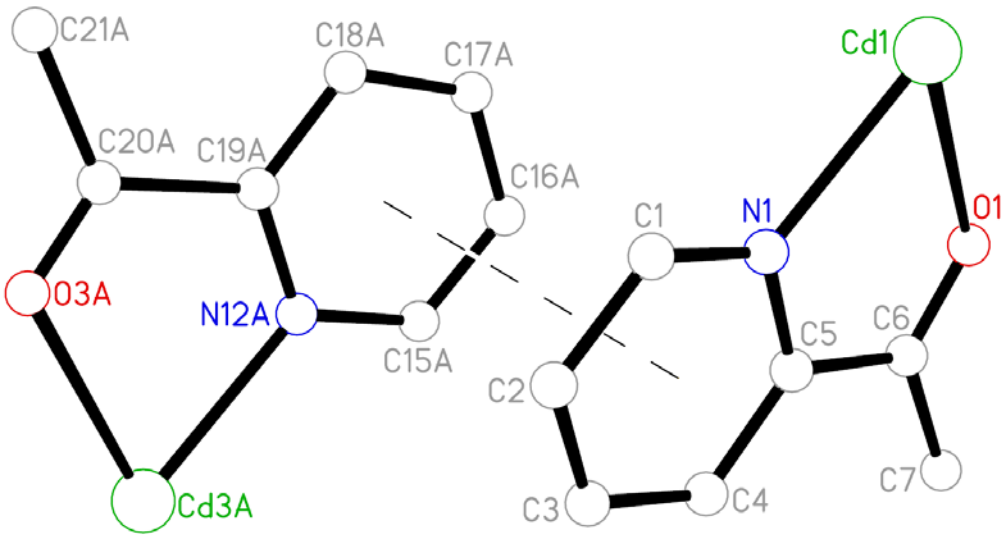
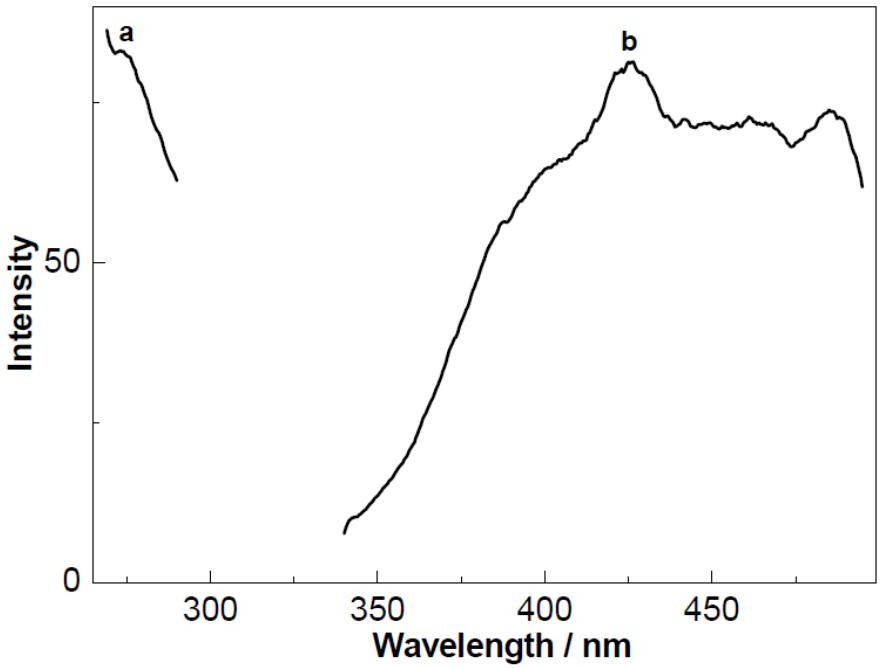
Cd(1)–N(3)	2.251(4)	Cd(4)–N(20)	2.547(4)
Cd(1)–N(38A)	2.268(4)	Cd(5)–N(26)	2.330(4)
Cd(1)–N(1)	2.281(4)	Cd(5)–N(14)	2.355(4)
Cd(1)–N(2)	2.303(4)	Cd(5)–N(20)	2.360(4)
Cd(1)–O(2)	2.443(3)	Cd(6)–N(32)	2.283(4)
Cd(1)–O(1)	2.475(4)	Cd(6)–N(6A)	2.314(4)
Cd(2)–N(9)	2.298(4)	Cd(6)–N(38)	2.316(4)
Cd(2)–N(6)	2.327(4)	Cd(6)–N(41)	2.347(4)
Cd(2)–N(17)	2.333(4)	Cd(6)–N(26)	2.439(4)
Cd(2)–N(3)	2.339(4)	Cd(6)–N(14A)	2.472(4)
Cd(2)–N(20)	2.374(4)	Cd(7)–N(35)	2.265(4)
Cd(2)–N(14)	2.404(4)	Cd(7)–N(29)	2.298(4)
Cd(3)–N(9)	2.260(4)	Cd(7)–N(41)	2.299(4)
Cd(3)–N(23)	2.268(4)	Cd(7)–N(44)	2.374(4)
Cd(3)–N(12)	2.292(4)	Cd(7)–N(45)	2.404(4)
Cd(3)–N(13)	2.347(4)	Cd(7)–O(5)	2.454(4)
Cd(3)–O(3)	2.437(4)	Cd(8)–N(45)	2.252(4)
Cd(3)–O(4)	2.503(4)	Cd(8)–N(48)	2.293(5)
Cd(4)–N(32)	2.292(4)	Cd(8)–N(51)	2.301(9)
Cd(4)–N(17)	2.311(4)	Cd(8)–N(35)	2.311(4)
Cd(4)–N(23)	2.327(4)	Cd(8)–N(48B)	2.373(4)
Cd(4)–N(29)	2.329(4)	Cd(8)–O(6)	2.539(8)
Cd(4)–N(26)	2.427(4)		
N(3)–Cd(1)–N(38A)	104.76(15)	N(23)–Cd(4)–N(20)	88.93(13)
N(3)–Cd(1)–N(1)	96.25(14)	N(29)–Cd(4)–N(20)	162.06(13)
N(38A)–Cd(1)–N(1)	104.98(16)	N(26)–Cd(4)–N(20)	75.26(12)
N(3)–Cd(1)–N(2)	95.68(15)	N(26)–Cd(5)–N(14)	97.76(13)
N(38A)–Cd(1)–N(2)	97.52(15)	N(26)–Cd(5)–N(14A)	82.24(13)
N(1)–Cd(1)–N(2)	150.84(15)	N(26)–Cd(5)–N(20A)	99.25(13)
N(3)–Cd(1)–O(2)	163.28(14)	N(14)–Cd(5)–N(20A)	96.47(13)
N(38A)–Cd(1)–O(2)	84.29(13)	N(26)–Cd(5)–N(20)	80.75(13)
N(1)–Cd(1)–O(2)	94.85(13)	N(14)–Cd(5)–N(20)	83.53(13)
N(2)–Cd(1)–O(2)	68.89(13)	N(14)–Cd(5)–N(14A)	180.00(13)
N(3)–Cd(1)–O(1)	86.66(14)	N(26)–Cd(5)–N(26A)	180.0
N(38A)–Cd(1)–O(1)	167.47(13)	N(20A)–Cd(5)–N(20)	180.00(11)
N(1)–Cd(1)–O(1)	68.01(15)	N(32)–Cd(6)–N(6A)	167.49(14)
N(2)–Cd(1)–O(1)	86.26(14)	N(32)–Cd(6)–N(38)	101.18(14)
O(2)–Cd(1)–O(1)	85.96(12)	N(6A)–Cd(6)–N(38)	89.74(15)
N(9)–Cd(2)–N(6)	94.62(14)	N(32)–Cd(6)–N(41)	89.67(15)
N(9)–Cd(2)–N(17)	94.91(14)	N(6A)–Cd(6)–N(41)	94.46(15)
N(6)–Cd(2)–N(17)	170.29(15)	N(38)–Cd(6)–N(41)	100.00(15)
N(9)–Cd(2)–N(3)	91.70(15)	N(32)–Cd(6)–N(26)	79.16(13)
N(6)–Cd(2)–N(3)	92.76(15)	N(6A)–Cd(6)–N(26)	88.72(14)
N(17)–Cd(2)–N(3)	88.81(14)	N(38)–Cd(6)–N(26)	165.16(13)
N(9)–Cd(2)–N(20)	93.78(14)	N(41)–Cd(6)–N(26)	94.84(14)
N(6)–Cd(2)–N(20)	97.08(14)	N(32)–Cd(6)–N(14A)	97.22(14)
N(17)–Cd(2)–N(20)	80.44(13)	N(6A)–Cd(6)–N(14A)	76.98(13)

N(3)–Cd(2)–N(20)	168.31(14)	N(38)–Cd(6)–N(14A)	87.55(13)
N(9)–Cd(2)–N(14)	171.12(14)	N(41)–Cd(6)–N(14A)	168.65(13)
N(6)–Cd(2)–N(14)	78.11(13)	N(26)–Cd(6)–N(14A)	77.73(12)
N(17)–Cd(2)–N(14)	92.23(13)	N(35)–Cd(7)–N(29)	93.20(16)
N(3)–Cd(2)–N(14)	93.73(14)	N(35)–Cd(7)–N(41)	113.55(16)
N(20)–Cd(2)–N(14)	82.19(13)	N(29)–Cd(7)–N(41)	98.24(16)
N(9)–Cd(3)–N(23)	103.70(15)	N(35)–Cd(7)–N(44)	148.64(16)
N(9)–Cd(3)–N(12)	110.96(14)	N(29)–Cd(7)–N(44)	103.93(14)
N(23)–Cd(3)–N(12)	100.51(15)	N(41)–Cd(7)–N(44)	90.07(15)
N(9)–Cd(3)–N(13)	91.16(15)	N(35)–Cd(7)–N(45)	75.49(15)
N(23)–Cd(3)–N(13)	94.64(15)	N(29)–Cd(7)–N(45)	166.89(15)
N(12)–Cd(3)–N(13)	149.01(15)	N(41)–Cd(7)–N(45)	92.45(15)
N(9)–Cd(3)–O(3)	87.50(14)	N(44)–Cd(7)–N(45)	83.54(14)
N(23)–Cd(3)–O(3)	167.43(14)	N(35)–Cd(7)–O(5)	86.82(15)
N(12)–Cd(3)–O(3)	69.67(14)	N(29)–Cd(7)–O(5)	91.16(14)
N(13)–Cd(3)–O(3)	90.76(14)	N(41)–Cd(7)–O(5)	156.84(14)
N(9)–Cd(3)–O(4)	149.68(14)	N(44)–Cd(7)–O(5)	67.06(14)
N(23)–Cd(3)–O(4)	98.12(14)	N(45)–Cd(7)–O(5)	81.76(14)
N(12)–Cd(3)–O(4)	85.00(13)	N(45)–Cd(8)–N(48)	108.47(17)
N(13)–Cd(3)–O(4)	66.09(14)	N(45)–Cd(8)–N(51)	144.1(3)
O(3)–Cd(3)–O(4)	73.74(13)	N(48)–Cd(8)–N(51)	107.4(3)
N(32)–Cd(4)–N(17)	165.20(14)	N(45)–Cd(8)–N(35)	77.61(15)
N(32)–Cd(4)–N(23)	96.26(14)	N(48)–Cd(8)–N(35)	102.37(16)
N(17)–Cd(4)–N(23)	86.35(14)	N(51)–Cd(8)–N(35)	93.9(2)
N(32)–Cd(4)–N(29)	97.12(15)	N(45)–Cd(8)–N(48B)	104.68(16)
N(17)–Cd(4)–N(29)	95.97(15)	N(48)–Cd(8)–N(48B)	78.00(19)
N(23)–Cd(4)–N(29)	107.41(15)	N(51)–Cd(8)–N(48B)	83.6(2)
N(32)–Cd(4)–N(26)	79.24(13)	N(35)–Cd(8)–N(48B)	177.47(17)
N(17)–Cd(4)–N(26)	94.18(13)	N(45)–Cd(8)–O(6)	76.5(2)
N(23)–Cd(4)–N(26)	163.61(14)	N(48)–Cd(8)–O(6)	166.6(2)
N(29)–Cd(4)–N(26)	88.85(14)	N(51)–Cd(8)–O(6)	68.8(3)
N(32)–Cd(4)–N(20)	88.16(13)	N(35)–Cd(8)–O(6)	90.8(2)
N(17)–Cd(4)–N(20)	77.31(13)	N(48B)–Cd(8)–O(6)	88.7(2)
Cd(1)–N(3)–Cd(2)	123.17(18)	Cd(5)–N(26)–Cd(4)	104.11(15)
Cd(6A)–N(6)–Cd(2)	105.80(17)	Cd(5)–N(26)–Cd(6)	100.78(14)
Cd(3)–N(9)–Cd(2)	118.33(18)	Cd(4)–N(26)–Cd(6)	95.95(13)
Cd(5)–N(14)–Cd(2)	96.73(13)	Cd(7)–N(29)–Cd(4)	129.5(2)
Cd(5)–N(14)–Cd(6A)	99.13(14)	Cd(6)–N(32)–Cd(4)	104.37(15)
Cd(2)–N(14)–Cd(6A)	98.78(14)	Cd(7)–N(35)–Cd(8)	104.56(19)
Cd(4)–N(17)–Cd(2)	105.02(16)	Cd(1A)–N(38)–Cd(6)	128.53(17)
Cd(5)–N(20)–Cd(2)	97.40(13)	Cd(7)–N(41)–Cd(6)	132.3(2)
Cd(5)–N(20)–Cd(4)	99.67(13)	Cd(8)–N(45)–Cd(7)	102.00(18)
Cd(2)–N(20)–Cd(4)	96.88(13)	Cd(8)–N(48)–Cd(8B)	102.00(19)
Cd(3)–N(23)–Cd(4)	126.73(18)		
Symmetry codes: A, 1–x, –y, 1–z; B, –x, –y, 2–z.			

5. Table S3 Selected structural parameters of supercubane clusters in cadmium halides CdI_2, $CdBr_2$ and $CdCl_2$, $[Cd_7N_{12}]$ unit in complex **1** and $[Cd_7O_{12}]$ unit in nonanuclear Cd_9 aggregate.

Supercubane structure $[Cd_7L_{12}]$	In CdI_2 (ICSD-9024)	In $CdBr_2$ (ICSD-31536)	In $CdCl_2$ (ICSD-30255)	$[Cd_7N_{12}]$ in **1** (this work)	$[Cd_7O_{12}]$ in Cd_9 aggregate (ref 10c)
Cd–L bond length (Å)	~2.986	~2.785	~2.658	~2.28–2.55	~2.16–2.34
Cd···Cd distance (Å)	~4.24	~3.99	~3.85	~3.56–3.75	~3.46–3.51
Cd–L–Cd angle (°)	~90.5	~91.3	~92.9	~96.0–105.8	~95.6–103.7
here L = I, Br, Cl, N or O.					

6. **Fig. S1** Intermolecular π–π stacking interaction between two pyridyl rings of 2-acetylpyridine ligands of adjacent chains in complex **1**. (Symmetry code A: 0.5+x, 0.5–y, z–0.5)



7. **Fig. S2** Solid state excitation spectra (a) and excited photoluminescent spectra (b) of complex **1**.