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Electronic Supplementary Information (ESI) for

A structural paradigm for 3-periodic semiregular ($4^6.6^9$)-hxg net with high-symmetry hexagonal geometry, constructed from the linear $[Cd_2NaO_6(H_2O)_6]$ SBUs and a flexible 6,6'-dithiodinicotinate linker

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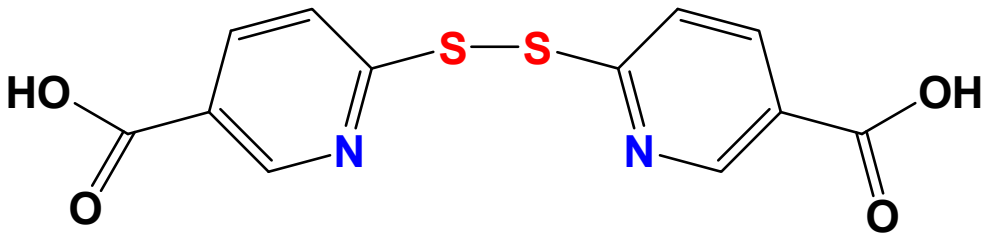
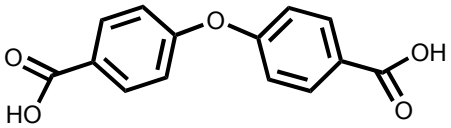
Chem. Commun.



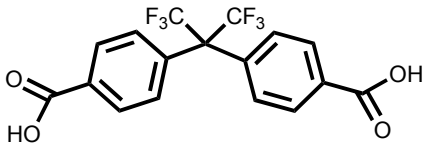
6,6'-dithiodinicotinic acid (H_2dtdn)

Chart S1. Chemical structure of the flexible H_2**dtdn** ligand.



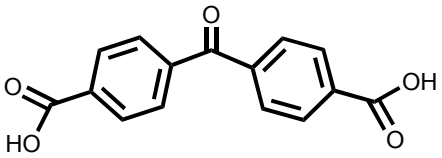
4,4'-oxydibenzoic acid

1. X.-L. Wang, C. Qin, E.-B. Wang, Y.-G. Li, Z.-M. Su, L. Xu and L. Carlucci, *Angew. Chem., Int. Ed*., 2005, **44**, 5824.
2. X.-L. Wang, C. Qin, E.-B. Wang, Y.-G. Li and Z.-M. Su, *Chem. Commun*., 2005, 5450.
3. Y. Ma, Z.-B. Han, Y.-K. He and L.-G. Yang, *Chem. Commun*., 2007, 4107.
4. P. Mahata, A. Sundaresan and S. Natarajan, *Chem. Commun*., 2007, 4471.
5. J. Zhang, S.-M. Chen and X.-H. Bu, *Angew. Chem., Int. Ed*., 2008, **47**, 5434.
6. P. Mahata, S. Natarajan, P. Panissod and M. Drillon, *J. Am. Chem. Soc*., 2009, **131**, 10140.



4,4'-(hexafluoroisopropylidene)bis(benzoic acid)

1. L. Pan, M. B. Sander, X.-Y. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath and J. K. Johnson, *J. Am. Chem. Soc*., 2004, **126**, 1308.
2. A. Monge, N. Snejko, E. Gutiérrez-Puebla, M. Medina, C. Cascales, C. Ruiz-Valero, M. Iglesias and B. Gómez-Lor, *Chem. Commun*., 2005, 1291.
3. L. Pan, D. H. Olson, L. R. Ciemnolonski, R. Heddy and J. Li, *Angew. Chem., Int. Ed*., 2006, **45**, 616.
4. B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jordá, H. García, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem., Int. Ed*., 2008, **47**, 1080.



4,4'-carbonyldibenzoic acid

1. X.-L. Wang, C. Qin, E.-B. Wang and Z.-M. Su, *Chem. Eur. J*., 2006, **12**, 2680.
2. D. Tanaka, K. Nakagawa, M. Higuchi, S. Horike, Y. Kubota, T. C. Kobayashi, M Takata and S. Kitagawa, *Angew. Chem., Int. Ed*., 2008, **47**, 3914.
3. H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc*., 2008, **130**, 11650.
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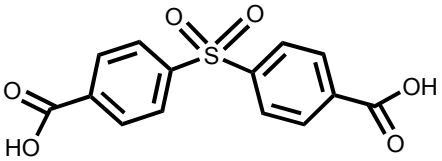
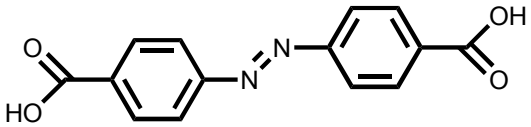
5. H. J. Park and M. P. Suh, *Chem. Commun*., 2010, **46**, 610.



4,4'-sulfonyldibenzoic acid

1. H. Furukawa, J. Kim, N. W. Ockwig and M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc*., 2008, **130**, 11650.
2. W.-J. Zhuang, H.-L. Sun, H.-B. Xu, Z.-M. Wang, S. Gao and L.-P. Jin, *Chem. Commun*., 2010, **46**, 4339.
3. D.-S. Li, F. Fu, J. Zhao, Y.-P. Wu, M. Du, K. Zou, W.-W. Dong and Y.-Y. Wang, *Dalton Trans*., 2010, **39**, 11522.



4,4'-azodibenzoic acid

1. T. M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc*., 2000, **122**, 4843.
2. P. S. Mukherjee, N. Das, Y. K. Kryschenko, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc*., 2004, **126**, 2464.
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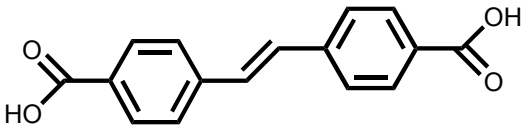
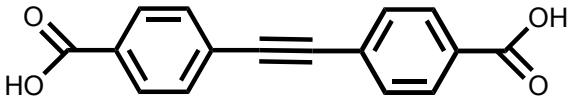
4. H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc*., 2008, **130**, 11650.



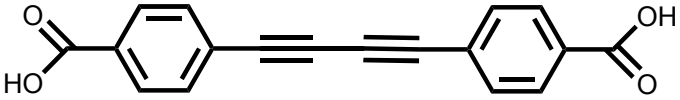
4,4'-stilbenedicarboxylic acid

1. C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons and M. D. Allendorf, *J. Am. Chem. Soc*., 2007, **129**, 7136.
2. A.-L. Cheng, N. Liu, Y.-F. Yue, Y.-W. Jiang, E.-Q. Gao, C.-H. Yan and M.-Y. He, *Chem. Commun*., 2007, 407.
3. J. Yang, J.-F. Ma, S. R. Batten and Z.-M. Su, *Chem. Commun*., 2008, 2233.



4,4'-ethyne-1,2-bis(benzoic acid)

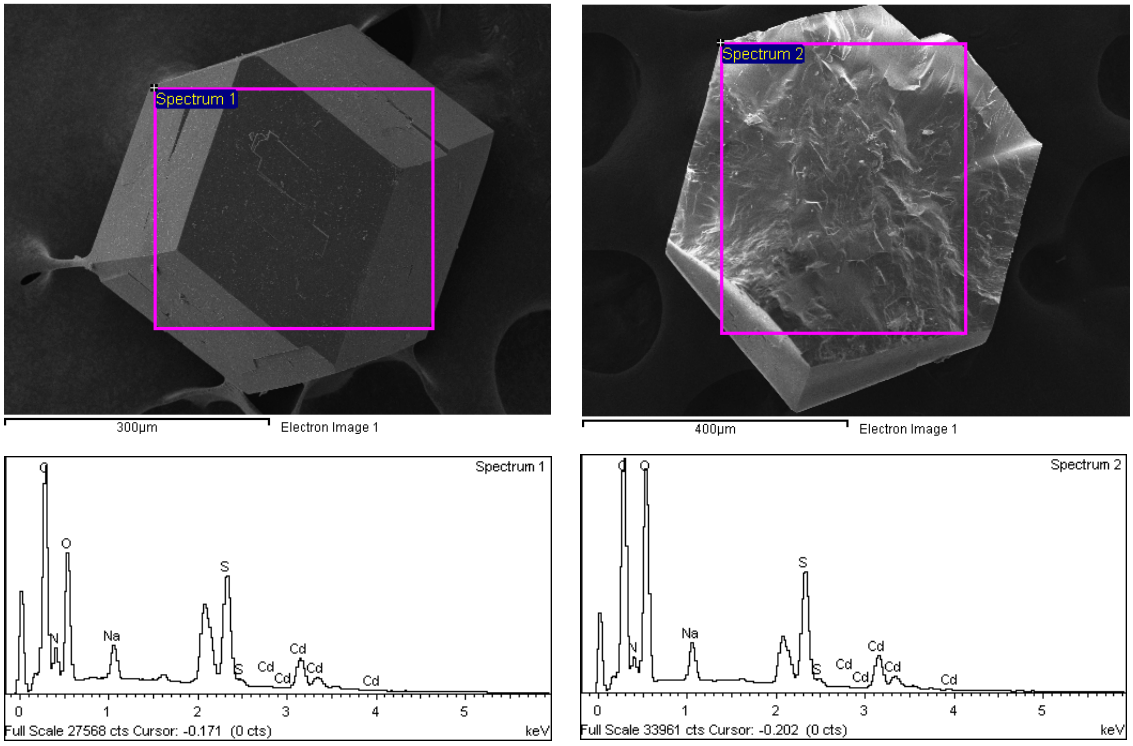
1. T. Gadzikwa, B.-S. Zeng, J. T. Hupp and S. T. Nguyen, *Chem. Commun*., 2008, 3672.
2. B. T. N. Pham, L. M. Lund and D.-T. Song, *Inorg. Chem*., 2008, **47**, 6329.



4,4'-diacetylene-1,4-bis(benzoic acid)

1. D. Britt, D. Tranchemontagne and O. M. Yaghi, *PNAS*., 2008, **105**, 11623.

Scheme S1 Eight 4,4'-dibenzoic acid ligands reported in the literatures with different spacers.



(a) **(b)**

Fig. S1 Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS) for (a) the surface and (b) the interior (after a single crystal is cut) of a crystal sample for **1**.

Results. The detected surface atom ratios for C, N, O, Na, S, and Cd are 31.93, 6.98, 29.73, 1.98, 13.41, and 15.97% and the corresponding interior atom ratios are 31.58, 5.85, 33.25, 1.43, 12.37, and 15.52% (calcd: C: 31.45, N: 6.11, O: 30.41, Na: 1.67, S: 13.99, and Cd: 16.35%). Notably, the experimental data (carried out on a JSM-6490 scanning electron microscope) shown herein are the mean value for ten pieces of crystals.

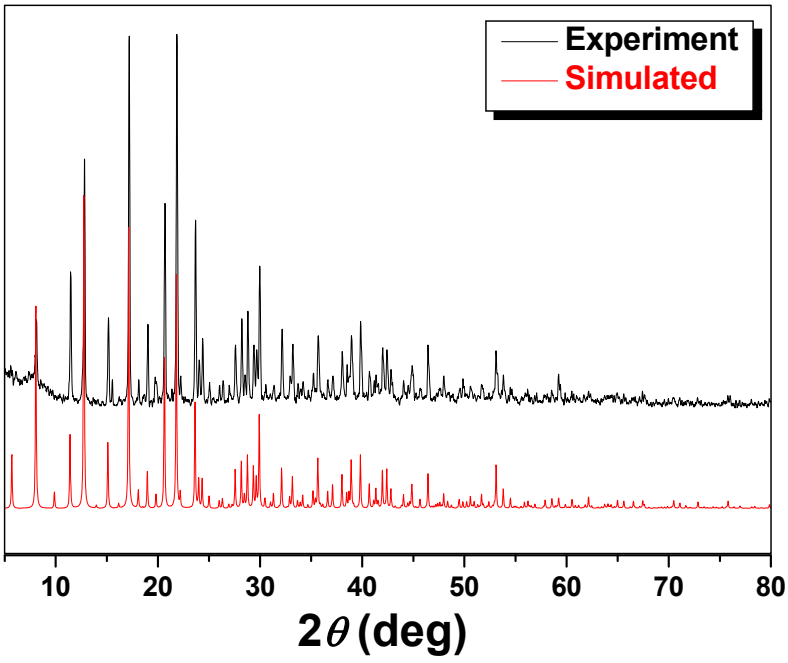
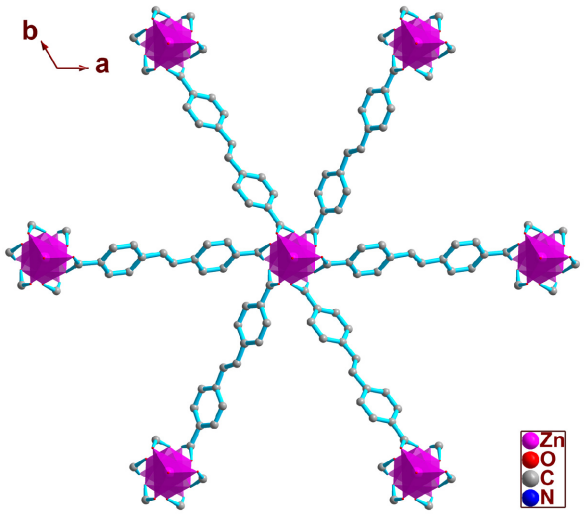
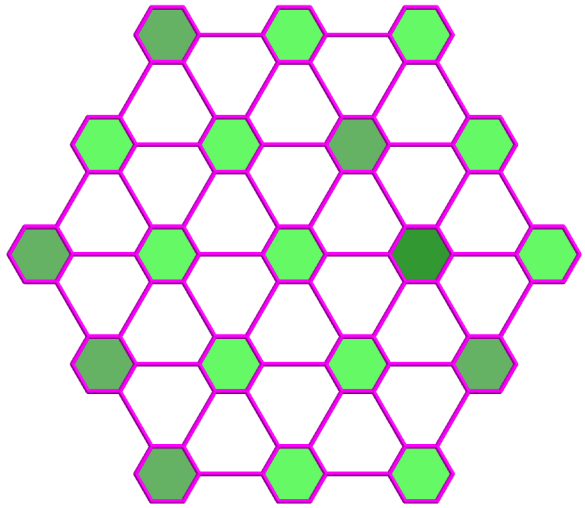


Fig. S2 X-ray powder diffraction (XRPD) pattern of **1**.



(a)



(b)

Fig. S3 (a) View of the 6-connected trinuclear Zn(II) cluster node (the coordinated DMF molecules are removed for clarity) and (b) the augmented 2-D 3^6 network (please see *ref. 3d* in the main text for details).

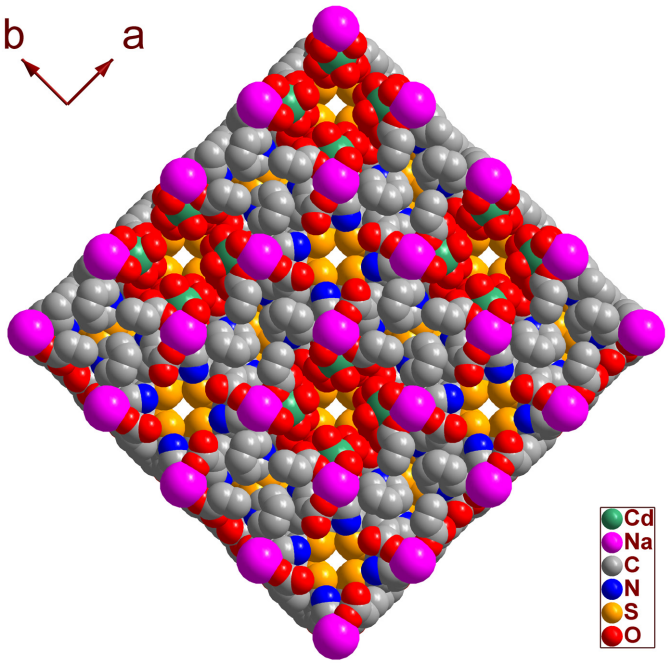


Fig. S4 Space-filling diagram of **1** viewed along the [001] direction.

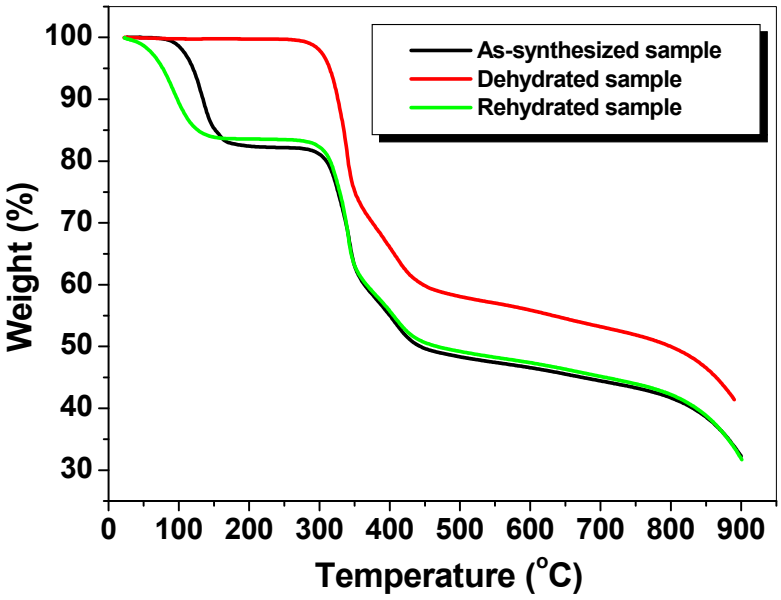


Fig. S5 Thermal gravimetric analysis (TGA) curve of **1** under different conditions.

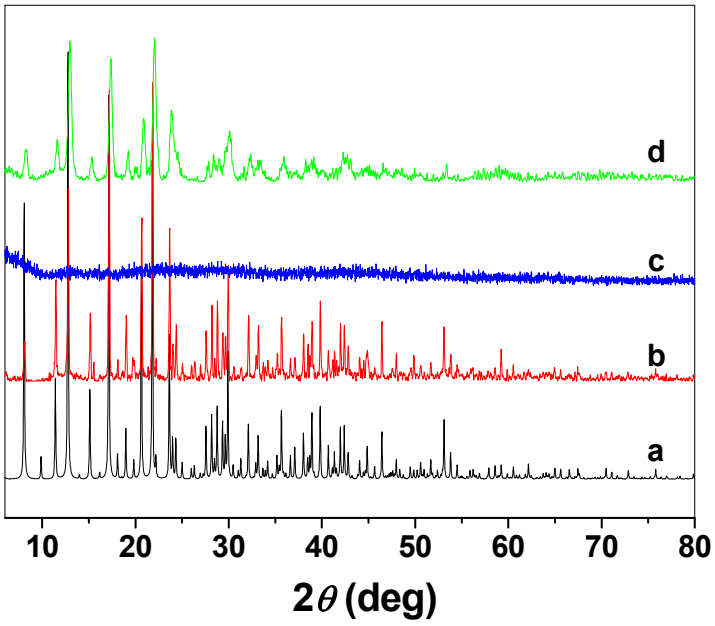
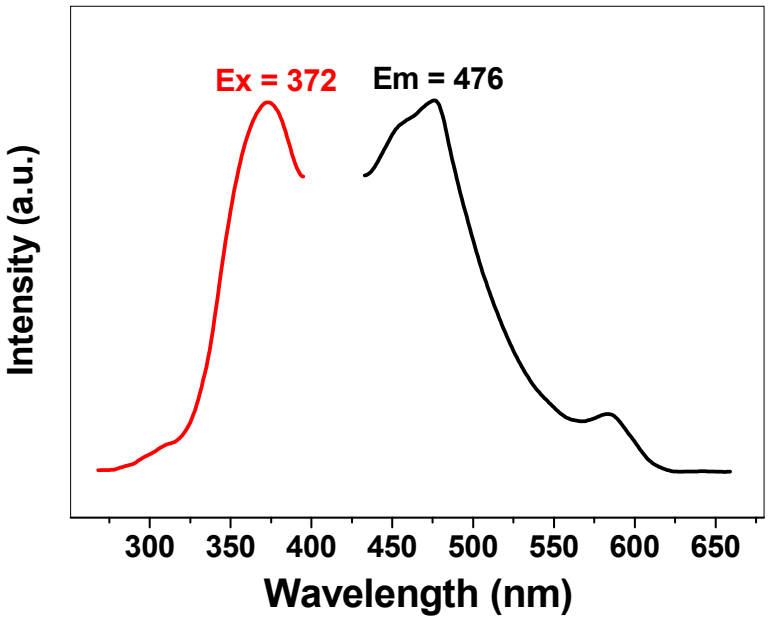
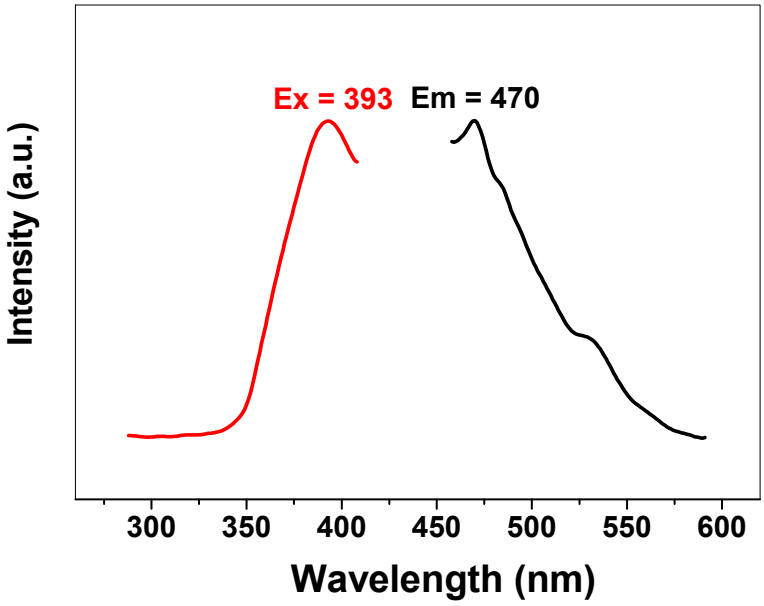


Fig. **6** XRPD patterns of **1**: (a) simulated pattern as well as experimental patterns for (b) the as-synthesized sample, (c) the dehydrated sample, and (d) the rehydrated sample.



(a)



(b)

Fig. S7 Solid-state excitation and emission spectra of (a) **1** and (b) the free **dtdn** ligand.

Table S1 Selected bond distances (Å) and bond angles (º) for **1**

Cd1–O3$^{\#1}$	2.285(3)	Cd1–O1$^{\#1}$	2.318(3)
Cd1–O3	2.285(3)	Cd1–O1	2.318(3)
Cd1–O3$^{\#2}$	2.285(3)	Cd1–O1$^{\#2}$	2.318(3)
Na1–O1	2.362(3)	Na1–O1$^{\#1}$	2.362(3)
O3$^{\#1}$–Cd1–O3	88.22(14)	O3$^{\#2}$–Cd1–O1	104.52(12)
O3$^{\#1}$–Cd1–O3$^{\#2}$	88.22(14)	O1$^{\#1}$–Cd1–O1	80.69(10)
O3–Cd1–O3$^{\#2}$	88.22(14)	O3$^{\#1}$–Cd1–O1$^{\#2}$	104.52(12)
O3$^{\#1}$–Cd1–O1$^{\#1}$	87.84(11)	O3–Cd1–O1$^{\#2}$	166.53(12)
O3–Cd1–O1$^{\#1}$	104.52(12)	O3$^{\#2}$–Cd1–O1$^{\#2}$	87.84(11)
O3$^{\#2}$–Cd1–O1$^{\#1}$	166.53(12)	O1$^{\#1}$–Cd1–O1$^{\#2}$	80.69(10)
O3$^{\#1}$–Cd1–O1	166.53(12)	O1–Cd1–O1$^{\#2}$	80.69(10)
O3–Cd1–O1	87.84(11)	Cd1$^{\#3}$–Na1–Cd1	180
O1$^{\#3}$–Na1–O1	180	O1$^{\#1}$–Na1–O1	78.93(9)

Symmetry codes: #1 = $-z + 1/2, -x + 1/2, y$; #2 = $-y + 1/2, z, -x + 1/2$; #3 = $-x + 1, -y, -z$.