Supporting Information

Designable Assembly of Atomically Precise $\text{Al}_4\text{O}_4$ Cubane Supported Mesoporous Heterometallic Architectures

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1. The supertetrahedral clusters and 2-fold interpenetrated frameworks in AlOC-99 to AlOC-108.

Fig. S1. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-99; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-99; (c) The 2-fold interpenetrated structure of AlOC-99.

Fig. S2. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-100; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-100; (c) The 2-fold interpenetrated structure of AlOC-100.

Fig. S3. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-101; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-101; (c) The 2-fold interpenetrated structure of AlOC-101.
Fig. S4. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-102; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-102; (c) The 2-fold interpenetrated structure of AlOC-102.

Fig. S5. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-103; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-103; (c) The 2-fold interpenetrated structure of AlOC-103.

Fig. S6. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-104; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-104; (c) The 2-fold interpenetrated structure of AlOC-104.
**Fig. S7.** (a) Structure of the heterometallic supertetrahedral cluster in AlOC-105; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-105; (c) The 2-fold interpenetrated structure of AlOC-105.

**Fig. S8.** (a) Structure of the heterometallic supertetrahedral cluster in AlOC-106; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-106; (c) The 2-fold interpenetrated structure of AlOC-106.

**Fig. S9.** (a) Structure of the heterometallic supertetrahedral cluster in AlOC-107; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-107; (c) The 2-fold interpenetrated structure of AlOC-107.
Fig. S10. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-108; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-108; (c) The 2-fold interpenetrated structure of AlOC-108.
2. The supertetrahedral clusters and non-interpenetrated frameworks in AlOC-109 to AlOC-111.

Fig. S11. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-109; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-109; (c) The non-interpenetrated structure of AlOC-109.

Fig. S12. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-110; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-110; (c) The non-interpenetrated structure of AlOC-110.

Fig. S13. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-111; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-111; (c) The non-interpenetrated structure of AlOC-111.
3. The supertetrahedral clusters and Ionsdaleite (lon) frameworks in AlOC-112 to AlOC-120.

Fig. S14. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-112; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-112; (c) The non-interpenetrated 3D topological structure of AlOC-112.

Fig. S15. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-113; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-113; (c) The non-interpenetrated 3D topological structure of AlOC-113.

Fig. S16. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-114; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-114; (c) The non-interpenetrated 3D topological structure of AlOC-114.
Fig. S17. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-115; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-115; (c) The non-interpenetrated 3D topological structure of AlOC-115.

Fig. S18. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-116; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-116; (c) The non-interpenetrated 3D topological structure of AlOC-116.

Fig. S19. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-117; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-117; (c) The non-interpenetrated 3D topological structure of AlOC-117.

Fig. S20. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-118; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-118; (c) The non-interpenetrated 3D topological structure of AlOC-118.
Fig. S21. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-119; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-119; (c) The non-interpenetrated 3D topological structure of AlOC-119.

Fig. S22. (a) Structure of the heterometallic supertetrahedral cluster in AlOC-120; (b) 3D framework showing the arrangement of supertetrahedral clusters in AlOC-120; (c) The non-interpenetrated 3D topological structure of AlOC-120.
4. The detail coordination environment information for Al ion, Co ion and ligands in AlOC-99.

Fig. S23. The coordination environments of Al (a) and Co (b) ions. Colour code: Al green; Co pink; N blue; O red; C grey. H atoms are omitted for clarity.

Fig. S24. The coordination mode of benzoate. Colour code: Al green; Co pink; O red; C grey. H atoms are omitted for clarity.

Fig. S25. The face-capping view of the supertetrahedral cluster. Colour code: Al green; Co pink; O red; C grey. H atoms are omitted for clarity.
Fig. S26. The comparison of hydrogen bonds in different chelated ligands modified frameworks. (a) and (b) The hydrogen bond positions and lengths in AlOC-99 (a) and AlOC-100 (b); (c) and (d) the hydrogen bond positions and lengths in AlOC-99 (c) and AlOC-101 (d), the dotted yellow line indicates that the bond length is too long to form hydrogen bond in AlOC-99; (e) and (f) the hydrogen bond positions and lengths in AlOC-115 (e) and AlOC-112 (f), the dotted yellow line indicates that the bond length is too long to form hydrogen bond in AlOC-112. Colour code: Al green; Co pink; O red; C grey; F orange. H atoms are omitted for clarity.

Fig. S27. The size of the different supertetrahedral cluster. Colour code: Al green; Cd turquoise; Mn violet; Fe yellow; Zn lavender; Co pink; O red; C grey. H atoms are omitted for clarity.
5. The packing of supertetrahedral cluster in AlOC-112.

**Fig. S28.** View of the 3D frameworks of AlOC-112 along the a axis (a), b axis (b) and c axis (c).

6. The mesoporous cavity in non-interpenetrated diamond (dia) frameworks.

**Fig. S29.** The view of 1D nanotubes along the a axis (a), b axis (b) and c axis (c).

**Fig. S30.** The diamond (dia) cavity in AlOC-109 (a), AlOC-110 (b) and AlOC-111 (c).
7. The N\textsubscript{2} and CO\textsubscript{2} sorption isotherms of AlOC-99, AlOC-109 and AlOC-112.

Fig. S31. (a) N\textsubscript{2} sorption isotherms of AlOC-99 at 77K; (b) CO\textsubscript{2} sorption isotherms of AlOC-99 at 273K; (c) CO\textsubscript{2} sorption isotherms of AlOC-99 at 298K; (d) N\textsubscript{2} sorption isotherms of AlOC-109 at 77K; (e) CO\textsubscript{2} sorption isotherms of AlOC-109 at 273K; (f) CO\textsubscript{2} sorption isotherms of AlOC-109 at 298K; (g) N\textsubscript{2} sorption isotherms of AlOC-112 at 77K; (h) CO\textsubscript{2} sorption isotherms of AlOC-112 at 273K; (i) CO\textsubscript{2} sorption isotherms of AlOC-112 at 298K.
8. The stabilities and hydrophobic properties of AIOC-99, AIOC-109 and AIOC-112.

Fig. S32. The TGA curves of AIOC-99 (a), AIOC-109 (b) and AIOC-112 (c) measured in N\textsubscript{2}/O\textsubscript{2} from room temperature to 800 °C.

Fig. S33. In-situ temperature-dependent PXRD patterns for AIOC-99 (a), AIOC-109 (b) and AIOC-112 (c).

Fig. S34. The PXRD patterns of AIOC-99, AIOC-109 and AIOC-112 after immersing in H\textsubscript{2}O or TEOA solution.
Fig. S35. The PXRD patterns of AlOC-99 (a and b) and AlOC-109 (c and d) after soaking in aqueous solution with different pH value for 24h.

Fig. S36. The PXRD patterns of AlOC-99 (a), AlOC-109 (b) and AlOC-112 (c) after soaking in different organic solvents at room temperature for 24h.
Fig. S37. The contact angle measurements of AlOC-99 (a), AlOC-109 (b) and AlOC-112 (c).

Fig. S38. The digital photo of AlOC-99 floating on the water. Although the density of AlOC-99 is larger than water, the crystals can still float on the surface of water indicating there are strong surface tension and interface hydrophobic.
Fig. S39. The PXRD patterns of AlOC-99, AlOC-109 and AlOC-112 after exposed in air for more than one year.

Fig. S40. The structure of Co$_2$Bdc$_2$Dabco (a) reported in literature and the coordination environment of Co in Co$_2$Bdc$_2$Dabco (b).
9. PXRD analyses.

Fig. S41. The PXRD patterns of two-fold interpenetrated diamond (dia) frameworks (simulated, black; experimental, red).
**Fig. S42.** The PXRD patterns of non-interpenetrated diamond (dia) frameworks (simulated, black; experimental, red).

**Fig. S43.** The PXRD patterns of non-interpenetrated lonsdaleite (lon) frameworks (simulated, black; experimental, red).

**Discussion for PXRD patterns:**
The experimental PXRD patterns for AIOC-99 to AIOC-120 are consistent with the simulated ones from single-crystal X-ray diffraction, which indicates that the samples are pure (Fig. S41–S43). The differences in indendity between the experimental and simulated patterns might be due to the variation in crystal orientation for power samples.
10. FT-IR spectra.

Fig. S44. The IR spectra of two-fold interpenetrated diamond (dia) frameworks.
Discussion for IR spectra:
The IR spectra have been recorded in the range of 3900–400 cm$^{-1}$ from solid samples palletized with KBr, which are presented in Fig. S44–S46. In the high wavenumber region ($\nu > 1000$ cm$^{-1}$), the weak absorption bands at 3097–3060 cm$^{-1}$, 2920–2893 cm$^{-1}$ can be ascribed to the stretching vibration modes of C–H bonds in aromatic rings, methylene or methyl groups. The characteristic stretching vibrations $\nu$(CO$_2^-$) of in carboxylic groups and $\nu$(C=C) in benzene rings are overlapped from 1622 cm$^{-1}$ to 1407 cm$^{-1}$. Among them, the asymmetric stretching vibration ($\nu_{as}$) and symmetric stretching vibration ($\nu_{s}$) of the carboxylate group can be clearly attributed, namely, the band at 1622–1566 cm$^{-1}$ is assigned to the $\nu_{as}$(CO$_2^-$) whilst the signal at 1448–1407 cm$^{-1}$ is ascribed to the $\nu_{s}$(CO$_2^-$). Besides, the intense absorption peaks appearing at 1099–1001 cm$^{-1}$ are assigned to the stretching vibrations of C–N from DABCO. In the low wavenumber region ($\nu < 1000$ cm$^{-1}$), the absorptions in the region ca. 900–650 cm$^{-1}$ for AIOC-99 to AIOC-120 can be attributed to the C–H in-plane or out-of-plane bends, ring breathing, and ring deformation absorptions of benzoates.
11. The EDS spectra.

![AIOC-99 EDS spectrum](image1)

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 52.23 | 65.24 |
| O        | 30.25 | 28.36 |
| N        | 0.53  | 0.57  |
| Co       | 12.01 | 3.06  |
| Al       | 4.98  | 2.77  |

Fig. S47. The EDS spectrum and quantitative analysis of AIOC-99.

![AIOC-100 EDS spectrum](image2)

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 53.50 | 67.42 |
| O        | 19.47 | 18.42 |
| F        | 10.63 | 8.47  |
| Co       | 11.38 | 2.87  |
Fig. S48. The EDS spectrum and quantitative analysis of AIOC-100.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 48.66 | 62.42 |
| O        | 25.79 | 24.83 |
| F        | 8.62  | 6.99  |
| Co       | 12.62 | 3.30  |
| Al       | 4.31  | 2.46  |

Fig. S49. The EDS spectrum and quantitative analysis of AIOC-101.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 54.81 | 67.65 |
| O        | 21.30 | 19.74 |
| F        | 9.54  | 7.44  |
| Co       | 9.13  | 2.30  |
Table:

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 48.07 | 61.11 |
| O        | 34.50 | 32.93 |
| Co       | 12.71 | 3.29  |
| Al       | 4.72  | 2.67  |

Fig. S50. The EDS spectrum and quantitative analysis of AlOC-102.

Fig. S51. The EDS spectrum and quantitative analysis of AlOC-103.

Fig. S52. The EDS spectrum and quantitative analysis of AlOC-104.
Fig. S53. The EDS spectrum and quantitative analysis of AIOC-105.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 42.14 | 58.89 |
| O        | 23.43 | 24.58 |
| S        | 19.55 | 10.24 |
| Co       | 8.78  | 2.50  |
| Al       | 6.10  | 3.79  |

Fig. S54. The EDS spectrum and quantitative analysis of AIOC-106.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 50.74 | 63.06 |
| O        | 33.65 | 31.40 |
| Mn       | 10.98 | 2.98  |
| Al       | 4.63  | 2.56  |
Table 5. The EDS spectrum and quantitative analysis of AlOC-107.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 56.14 | 66.43 |
| O        | 33.72 | 29.86 |
| N        | 0.41  | 0.27  |
| Fe       | 3.58  | 1.88  |
| Al       | 6.15  | 1.56  |

Fig. S55. The EDS spectrum and quantitative analysis of AlOC-107.

Table 6. The EDS spectrum and quantitative analysis of AlOC-108.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 59.70 | 74.65 |
| O        | 19.69 | 18.48 |
| Zn       | 14.10 | 3.24  |
| Al       | 6.51  | 3.63  |

Fig. S56. The EDS spectrum and quantitative analysis of AlOC-108.
### EDS Spectrum and Quantitative Analysis of AlOC-109

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 62.27 | 74.98 |
| O        | 22.07 | 19.95 |
| Co       | 11.43 | 2.81  |
| Al       | 4.23  | 2.26  |

**Fig. S57.** The EDS spectrum and quantitative analysis of AlOC-109.

### EDS Spectrum and Quantitative Analysis of AlOC-110

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 52.76 | 66.29 |
| O        | 28.59 | 26.97 |
| Fe       | 12.76 | 3.45  |
| Al       | 5.89  | 3.29  |

**Fig. S58.** The EDS spectrum and quantitative analysis of AlOC-110.
| Elements | Wt. %  | Mol.% |
|----------|--------|-------|
| C        | 55.31  | 73.30 |
| O        | 21.02  | 20.91 |
| Cd       | 18.24  | 2.58  |
| Al       | 5.43   | 3.21  |

Fig. S59. The EDS spectrum and quantitative analysis of AlOC-111.

| Elements | Wt. %  | Mol.% |
|----------|--------|-------|
| C        | 58.34  | 70.50 |
| O        | 26.49  | 24.03 |
| Co       | 9.21   | 2.27  |
| Al       | 5.96   | 3.20  |

Fig. S60. The EDS spectrum and quantitative analysis of AlOC-112.
| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 54.67 | 69.02 |
| O        | 15.92 | 15.09 |
| F        | 12.37 | 9.87  |
| Co       | 11.66 | 3.00  |
| Al       | 5.38  | 3.02  |

**Fig. S61.** The EDS spectrum and quantitative analysis of **AIOC-113**.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 49.42 | 68.41 |
| O        | 15.84 | 16.46 |
| Cl       | 19.66 | 9.22  |
| Co       | 10.12 | 2.86  |
| Al       | 4.96  | 3.05  |

**Fig. S62.** The EDS spectrum and quantitative analysis of **AIOC-114**.
| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 59.65 | 72.18 |
| O        | 23.75 | 21.57 |
| N        | 1.22  | 1.27  |
| Co       | 11.30 | 2.79  |
| Al       | 4.08  | 2.19  |

**Fig. S63.** The EDS spectrum and quantitative analysis of AlOC-115.

| Elements | Wt. % | Mol.% |
|----------|-------|-------|
| C        | 54.29 | 66.80 |
| O        | 21.33 | 19.70 |
| N        | 7.68  | 8.10  |
| Co       | 12.66 | 3.18  |
| Al       | 4.04  | 2.22  |

**Fig. S64.** The EDS spectrum and quantitative analysis of AlOC-116.
| Elements | Wt. %  | Mol.% |
|----------|--------|-------|
| C        | 59.24  | 73.30 |
| O        | 20.96  | 19.47 |
| Mn       | 13.11  | 3.55  |
| Al       | 6.69   | 3.68  |

Fig. S65. The EDS spectrum and quantitative analysis of AlOC-117.

| Elements | Wt. %  | Mol.% |
|----------|--------|-------|
| C        | 60.86  | 70.85 |
| O        | 29.61  | 25.88 |
| Fe       | 6.21   | 1.55  |
| Al       | 3.32   | 1.72  |

Fig. S66. The EDS spectrum and quantitative analysis of AlOC-118.
| Elements | Wt. % | Mol. % |
|----------|-------|--------|
| C        | 59.42 | 74.55  |
| O        | 19.69 | 18.55  |
| Zn       | 14.52 | 3.35   |
| Al       | 6.37  | 3.55   |

Fig. S67. The EDS spectrum and quantitative analysis of AIOC-119.

| Elements | Wt. % | Mol. % |
|----------|-------|--------|
| C        | 57.39 | 77.59  |
| O        | 15.40 | 15.63  |
| Cd       | 20.97 | 3.03   |
| Al       | 6.24  | 3.75   |

Fig. S68. The EDS spectrum and quantitative analysis of AIOC-120.

Discussion for EDS spectra:
The EDS spectra of AIOC-99 to AIOC-120 were used to confirm the existence of metal elements. Also, the quantification of metal elements was determined (Fig. S47–S68). The molar ratios between Al and M are approximately 1, which are consistent with the formula.
12. The XPS spectra.

Fig. S69. The Co 2p and Al 2p XPS spectra of AlOC-99, Co(Ac)$_2$·4H$_2$O and Al(OiPr)$_3$.

Fig. S70. The Co 2p and Al 2p XPS spectra of AlOC-100, Co(Ac)$_2$·4H$_2$O and Al(OiPr)$_3$.

Fig. S71. The Co 2p and Al 2p XPS spectra of AlOC-101, Co(Ac)$_2$·4H$_2$O and Al(OiPr)$_3$. 
Fig. S72. The Co 2p and Al 2p XPS spectra of AlOC-102, Co(Ac)$_2$·4H$_2$O and Al(O'Pr)$_3$.

Fig. S73. The Co 2p and Al 2p XPS spectra of AlOC-103, Co(Ac)$_2$·4H$_2$O and Al(O'Pr)$_3$.

Fig. S74. The Co 2p and Al 2p XPS spectra of AlOC-104, Co(Ac)$_2$·4H$_2$O and Al(O'Pr)$_3$.

Fig. S75. The Co 2p and Al 2p XPS spectra of AlOC-105, Co(Ac)$_2$·4H$_2$O and Al(O'Pr)$_3$. 
Fig. S76. The Mn 2p, Mn 3s and Al 2p XPS spectra of AlOC-106, MnCl₂·4H₂O and Al(O'Pr)₃.

Fig. S77. The Fe 2p and Al 2p XPS spectra of AlOC-107, FeCl₃ and Al(O'Pr)₃.

Fig. S78. The Zn 2p and Al 2p XPS spectra of AlOC-108, Zn(Ac)₂·2H₂O and Al(O'Pr)₃.

Fig. S79. The Co 2p and Al 2p XPS spectra of AlOC-109, Co(Ac)₂·4H₂O and Al(O'Pr)₃.
Fig. S80. The Fe 2p and Al 2p XPS spectra of AlOC-110, FeCl₃ and Al(OPr)₃.

Fig. S81. The Cd 3d and Al 2p XPS spectra of AlOC-111, Cd(Ac)₂·2H₂O and Al(OPr)₃.

Fig. S82. The Co 2p and Al 2p XPS spectra of AlOC-112, Co(Ac)₂·4H₂O and Al(OPr)₃.

Fig. S83. The Co 2p and Al 2p XPS spectra of AlOC-113, Co(Ac)₂·4H₂O and Al(OPr)₃.
Fig. S84. The Co 2p and Al 2p XPS spectra of AlOC-114, Co(Ac)$_2$·4H$_2$O and Al(OPr)$_3$.

Fig. S85. The Co 2p and Al 2p XPS spectra of AlOC-115, Co(Ac)$_2$·4H$_2$O and Al(OPr)$_3$.

Fig. S86. The Co 2p and Al 2p XPS spectra of AlOC-116, Co(Ac)$_2$·4H$_2$O and Al(OPr)$_3$.

Fig. S87. The Mn 2p, Mn 3s and Al 2p XPS spectra of AlOC-117, MnCl$_2$·4H$_2$O and Al(OPr)$_3$. 
**Fig. S88.** The Fe 2p and Al 2p XPS spectra of AlOC-118, FeCl₃ and Al(OiPr)₃.

**Fig. S89.** The Zn 2p and Al 2p XPS spectra of AlOC-119, Zn(Ac)₂·2H₂O and Al(OiPr)₃.

**Fig. S90.** The Cd 3d and Al 2p XPS spectra of AlOC-120, Cd(Ac)₂·2H₂O and Al(OiPr)₃.

**Discussion for XPS spectra:**

The XPS measurements of AlOC-99 to AlOC-120 were conducted to verify the valence states of metal ions in frameworks. The high-resolution Co 2p spectra exhibit two main regions of Co 2p₁/₂ and Co 2p₃/₂ with ca. 16 eV binding energy difference (Fig. S69–S75, S79, and S82–S86).[1-2] In Co 2p₁/₂ region, it can be deconvoluted into two peaks of Co²⁺ at 796.7–797.3 eV and the corresponding shake-up satellite peak at 801.8–802.7 eV. Similarly, Co 2p₃/₂ region also demonstrates two peaks of Co²⁺ (780.8–781.4 eV) and a relevant satellite peak (785.8–786.4 eV). The two satellite peaks are assigned to the shake-up excitation of high-spin Co²⁺ ions. The Mn 2p spectra of AlOC-106 and AlOC-117 are split into two components at 641.6–642.1 eV (Mn 2p₃/₂) and 654.1–654.2 eV (Mn 2p₁/₂), with a satellite peak located at 647.1–647.3 eV (Fig. S76 and S87).[3] These binding energies are consistent with an Mn²⁺ cation as reported for manganese oxide.[4] The Mn 3s core peak allows us to confirm the oxidation of Mn.[5] The splitting of this peak is dependent on the number of 3d electrons, and expected values are ~6.5 eV for Mn⁵⁺, ~5.5 eV for Mn⁴⁺, and ~4.5 eV for Mn³⁺. Here, the splitting value for AlOC-106 and AlOC-117 are respectively ~6.1 eV and 6.4 eV (Fig. S76b and S87b), indicated the existence of Mn²⁺ in crystals. For AlOC-108 and AlOC-119, the observed Zn 2p₁/₂ and Zn 2p₃/₂ are located at 1044.6–1044.8 eV and 1021.5–1021.8 eV, corresponding to Zn²⁺ species (Fig. S78 and S89).[6-7] In Fig. S81 and S90, two peaks locate at about 411.3–411.5 eV and 404.5–404.7 eV, matched well with the spin-orbit separation between Cd 3d₃/₂ and Cd 3d₅/₂ of Cd²⁺ in frameworks.[8] The Fe XPS analysis for AlOC-107, AlOC-110 and AlOC-118 were also researched, however, the obvious Fe³⁺ signals were captured (Fig. S77, S80 and S88), which is inconsistency with BVS results.[9] This maybe owing to the rapid oxidation of external Fe³⁺ species when freshly prepared crystals were exposed into air. The Al 2p signals only contain one peak centered at 73.9–74.3 eV, consistent with the literature value for Al³⁺.[10] Besides, the characteristic XPS peaks of AlOC-99 to AlOC-120 are in agreement with pure metal salts and Al(OiPr)₃.
13. The UV-vis absorption spectra and Tau plots.

Fig. S91. The crystal colour of AlOC-110 before and after exposing in air.

Fig. S92. The UV-vis absorption spectra.

Fig. S93. Tau plots of two-fold interpenetrated diamond (dia) frameworks based on UV-vis diffuse reflectance spectra.
Fig. S94. Tau plots of non-interpenetrated diamond (dia) frameworks based on UV-vis diffuse reflectance spectra.

Fig. S95. Tau plots of non-interpenetrated lonsdaleite (lon) frameworks based on UV-vis diffuse reflectance spectra.

14. Catalytic stability.

Fig. S96. PXRD patterns of AIOC-99, AIOC-109 and AIOC-112 after catalysis.
Table S1. Crystallographic data and structure refinement parameters for two-fold interpenetrated diamond (dia) frameworks (AlOC-99 to AlOC-103).

|                  | AlOC-99   | AlOC-100  | AlOC-101  | AlOC-102  | AlOC-103  |
|------------------|-----------|-----------|-----------|-----------|-----------|
| Empirical formula| C_{96}H_{84}Al_{4}Co_{4}N_{4}O_{28} | C_{96}H_{84}Al_{4}Co_{4}N_{4}O_{28} | C_{96}H_{84}Al_{4}Co_{4}N_{4}O_{28} | C_{96}H_{84}Al_{4}Co_{4}N_{4}O_{28} | C_{72}H_{60}Al_{4}Co_{4}N_{4}O_{28} |
| Formula weight   | 2085.39   | 2301.30   | 2301.21   | 2301.21   | 1964.96   |
| Temperature / K   | 105.61(11) K | 106.15(10) K | 105.66(11) K | 105.94(10) K | 105.63(19) K |
| Crystal system    | Cubic     | Cubic     | Cubic     | Cubic     | Cubic     |
| Space group       | Fd-3c     | Fd-3c     | Fd-3c     | Fd-3c     | Fd-3c     |
| a [Å]            | 32.2520(2) | 32.1911(2) | 32.3063(3) | 32.7575(6) | 31.6599(6) |
| b [Å]            | 32.2520(2) | 32.1911(2) | 32.3063(3) | 32.7575(6) | 31.6599(6) |
| c [Å]            | 32.2520(2) | 32.1911(2) | 32.3063(3) | 32.7575(6) | 31.6599(6) |
| α [°]            | 90        | 90        | 90        | 90        | 90        |
| β [°]            | 90        | 90        | 90        | 90        | 90        |
| γ [°]            | 90        | 90        | 90        | 90        | 90        |
| V [Å³]           | 33548.3(6) | 33358.6(6) | 33718.0(9) | 35150.6(19) | 31734.3(18) |
| Z                 | 15.99936  | 15.99936  | 16        | 16        | 15.99936  |
| \(\rho_{\text{calc}}\) [g cm\(^{-3}\)] | 1.651 | 1.833 | 1.813 | 1.739 | 1.645 |
| \(\mu\) [mm\(^{-1}\)] | 4.958 | 5.168 | 5.114 | 4.905 | 5.288 |
| F (000)          | 17152.0   | 18688.0   | 18688.0   | 18688.0   | 16000.0   |
| Index ranges     | −26 ≤ h ≤ 38 | −38 ≤ h ≤ 40 | −39 ≤ h ≤ 24 | −22 ≤ h ≤ 39 | −17 ≤ h ≤ 30 |
|                  | −41 ≤ k ≤ 39 | −26 ≤ k ≤ 33 | −40 ≤ k ≤ 25 | −21 ≤ k ≤ 36 | −39 ≤ k ≤ 21 |
|                  | −19 ≤ l ≤ 29 | −28 ≤ l ≤ 40 | −24 ≤ l ≤ 31 | −31 ≤ l ≤ 40 | −19 ≤ l ≤ 29 |
| Reflns collected | 10409     | 9217      | 9405      | 9910      | 9217      |
| unique reflns \([R_{int}]\) | 1586[0.0212] | 1435 [0.0223] | 1405 [0.0384] | 1503 [0.1526] | 1350[0.0507] |
| data/restraints/parameters | 1586/84/128   | 1435/78/160  | 1405/57/109  | 1503/37/101  | 1350/0/94  |
| GOF on \(F^2\)  | 1.056     | 1.126     | 1.077     | 1.146     | 1.135     |
| \(R_p\), \(wR_p\) \([I > 2\sigma(I)]\) | 0.0801, 0.2357 | 0.0759, 0.2338 | 0.1149, 0.3019 | 0.1474, 0.3309 | 0.0998, 0.2250 |
| \(R_p\), \(wR_p\) \([all\ data]\) | 0.0878, 0.2444 | 0.0867, 0.2477 | 0.1415, 0.3286 | 0.2083, 0.3653 | 0.1427, 0.2526 |
| \(\Delta \rho_{\text{max}}/\rho_{\text{calc}}\) [eÅ\(^{-3}\)] | 1.03/−0.83 | 0.36/−0.58 | 1.23/−1.11 | 0.55/−0.71 | 0.97/−0.42 |
| CCDC number      | 2056099   | 2056100   | 2056101   | 2056102   | 2056103   |
Table S2. Crystallographic data and structure refinement parameters for two-fold interpenetrated diamond (dia) frameworks (AlOC-104 to AlOC-108).

|                  | AlOC-104                | AlOC-105                | AlOC-106                | AlOC-107                | AlOC-108                |
|------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| **Empirical formula** | C_{72}H_{60}Al_{4}Co_{4}N_{4}O_{28}S_{12} | C_{72}H_{60}Al_{4}Co_{4}N_{4}O_{28}S_{12} | C_{96}H_{84}Al_{4}Mn_{4}N_{4}O_{28} | C_{96}H_{84}Al_{4}Fe_{4}N_{4}O_{28} | C_{96}H_{84}Al_{4}Zn_{4}N_{4}O_{28} |
| **Formula weight** | 2157.68                 | 2157.68                 | 2069.35                 | 2073.07                 | 2111.15                 |
| **Temperature / K** | 105.84(14) K            | 105.89(10) K            | 293(2) K                | 99.99(10) K             | 108.44(10) K            |
| **Crystal system** | Cubic                   | Cubic                   | Cubic                   | Cubic                   | Cubic                   |
| **Space group**   | Fd-3c                   | Fd-3c                   | Fd-3c                   | Fd-3c                   | Fd-3c                   |
| **α [Å]**         | 32.0714(6)              | 32.3326(9)              | 32.8415(3)              | 32.3651(4)              | 32.2437(2)              |
| **β [Å]**         | 32.0714(6)              | 32.3326(9)              | 32.8415(3)              | 32.3651(4)              | 32.2437(2)              |
| **γ [Å]**         | 90                      | 90                      | 90                      | 90                      | 90                      |
| **V [Å³]**        | 32987.8(19)             | 33800(3)                | 35421.7(10)             | 33902.4(13)             | 33522.4(6)              |
| **Z**             | 15.99936                | 16                      | 16                      | 15.99936                | 15.99936                |
| **ρcalcd [g cm⁻³]** | 1.738                   | 1.696                   | 1.552                   | 1.625                   | 1.673                   |
| **μ [mm⁻¹]**      | 6.857                   | 6.692                   | 0.684                   | 4.367                   | 1.548                   |
| **F (000)**       | 17536.0                 | 17536.0                 | 17024.0                 | 17088.0                 | 17344.0                 |
| **Index ranges**  | -23 ≤ h ≤ 34            | -23 ≤ h ≤ 31            | -39 ≤ h ≤ 41            | -36 ≤ h ≤ 37            | -5 ≤ h ≤ 41             |
|                  | -38 ≤ k ≤ 40            | -24 ≤ k ≤ 38            | -41 ≤ k ≤ 41            | -34 ≤ k ≤ 20            | -19 ≤ k ≤ 31            |
|                  | -21 ≤ l ≤ 29            | -40 ≤ l ≤ 38            | -40 ≤ l ≤ 41            | -23 ≤ l ≤ 28            | -40 ≤ l ≤ 18            |
| **Refins collected** | 9190                    | 9024                    | 56347                   | 7286                    | 9994                    |
| **unique reflns [Rint]** | 1385 [0.0984]          | 1444 [0.0850]           | 1522 [0.0798]           | 1168 [0.0262]           | 1573 [0.0206]           |
| **data/restraints/parameters** | 1385/6/85               | 1444/12/94              | 1522/150/134            | 1168/219/136            | 1573/72/134             |
| **GOF on F²**     | 1.308                   | 1.097                   | 1.185                   | 1.051                   | 1.154                   |
| **R₁, wR₂ [I > 2σ(I)]** | 0.1447, 0.3634          | 0.1274, 0.3121          | 0.0858, 0.2422          | 0.0566, 0.1641          | 0.0548, 0.1676          |
| **R₁, wR₂ [all data]** | 0.2094, 0.4048          | 0.1813, 0.3512          | 0.0997, 0.2547          | 0.0715, 0.1779          | 0.0568, 0.1697          |
| **Δρmax/Δρmin(e·Å⁻³)** | 0.93/–0.75              | 0.98/–0.94              | 0.39/–0.46              | 0.40/–0.48              | 0.36/–0.43              |
| **CCDC number**   | 2056104                 | 2056105                 | 2056106                 | 2156657                 | 2056107                 |
Table S3. Crystallographic data and structure refinement parameters for non-interpenetrated diamond (dia) frameworks (AIOC-109 to AIOC-111).

|                  | AIOC-109          | AIOC-110          | AIOC-111          |
|------------------|-------------------|-------------------|-------------------|
| Empirical formula| $C_{108}H_{108}Al_{4}Co_{4}N_{4}O_{28}$ | $C_{96}H_{84}Al_{4}Fe_{4}N_{4}O_{28}$ | $C_{96}H_{84}Al_{4}Cd_{4}N_{4}O_{28}$ |
| Formula weight   | 2253.62           | 2072.99           | 2299.19           |
| Temperature / K  | 293(2) K          | 108.56(10) K      | 108.29(11) K      |
| Crystal system   | Cubic             | Cubic             | Cubic             |
| Space group      | $F_{4} \overline{3}d$ | $F_{4} \overline{3}d$ | $F_{4} \overline{3}d$ |
| $a$ [Å]          | 32.1474(2)        | 32.1100(6)        | 32.8932(3)        |
| $b$ [Å]          | 32.1474(2)        | 32.1100(6)        | 32.8932(3)        |
| $c$ [Å]          | 32.1474(2)        | 32.1100(6)        | 32.8932(3)        |
| $α$ [°]          | 90                | 90                | 90                |
| $β$ [°]          | 90                | 90                | 90                |
| $γ$ [°]          | 90                | 90                | 90                |
| $V$ [Å$^3$]      | 33222.9(6)        | 33107.1(19)       | 35589.2(10)       |
| $Z$              | 8                 | 8                 | 8                 |
| $\rho_{ave}$ [g cm$^{-3}$] | 0.901             | 0.832             | 0.858             |
| $\mu$ [mm$^{-1}$] | 2.520             | 2.236             | 2.882             |
| $F(000)$         | 9344.0            | 8544.0            | 9248.0            |
| Index ranges     | $-36 \leq h \leq 38$ | $-17 \leq h \leq 38$ | $-41 \leq h \leq 33$ |
|                  | $-36 \leq k \leq 30$ | $-24 \leq k \leq 28$ | $-38 \leq k \leq 42$ |
|                  | $-37 \leq l \leq 37$ | $-40 \leq l \leq 38$ | $-38 \leq l \leq 33$ |
| Reflections collected | 30287             | 10983             | 40255             |
| Independent reflections | 2554 [0.0400]     | 3067 [0.0465]     | 3395 [0.1600]     |
| data/restraints/parameters | 2554/37/112       | 3067/2/97         | 3395/18/103       |
| GOF on $F^{2}$   | 1.062             | 0.994             | 1.021             |
| $R_{1}$, w$R_{2}$ ($I > 2\sigma(I)$) | 0.0736, 0.2196    | 0.0634, 0.1836    | 0.0751, 0.1956    |
| $R_{1}$, w$R_{2}$ [all data] | 0.0882, 0.2409    | 0.1068, 0.2120    | 0.0810, 0.2001    |
| $Δρ_{ave}$/$Δρ_{max}$ (e·Å$^{-3}$) | 0.67/−0.31        | 0.45/−0.26        | 0.71/−0.62        |
| Flack parameter  | 0.085(18)         | 0.082(18)         | 0.463(13)         |
| CCDC number      | 2056108           | 2056109           | 2056110           |
Table S4. Crystallographic data and structure refinement parameters for lonsdaleite (Ion) frameworks (AIOC-112 to AIOC-120).

| Empirical formula | AIOC-112 | AIOC-113 | AIOC-114 | AIOC-115 | AIOC-116 | AIOC-117 | AIOC-118 | AIOC-119 | AIOC-120 |
|-------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Cubic HAlCo-N2O6  | 2085.33  | 2301.23  | 2498.64  | 2253.64  | 2265.52  | 2069.35  | 2073.01  | 2111.07  | 2299.21  |
| Temperature / K   | 298.83 K | 105.8(3) K | 106.22(10) K | 105.78(10) K | 109.8(3) K | 100.00(18) K | 100.00(14) K | 293(2) K | 108.30(10) K |
| Crystal system    | Hexagonal | Hexagonal | Hexagonal | Hexagonal | Hexagonal | Hexagonal | Hexagonal | Hexagonal | Hexagonal |
| Space group       | P-62c    | P-62c    | P-62c    | P-62c    | P-62c    | P-62c    | P-62c    | P-62c    | P-62c    |
| a [Å]             | 22.8201(6) | 22.6534(4) | 22.7823(2) | 22.6942(3) | 22.6772(3) | 22.9056(5) | 22.7862(8) | 22.8185(4) | 23.1974(5) |
| b [Å]             | 22.8201(6) | 22.6534(4) | 22.7823(2) | 22.6942(3) | 22.6772(3) | 22.9056(5) | 22.7862(8) | 22.8185(4) | 23.1974(5) |
| c [Å]             | 37.3225(10) | 37.1554(7) | 37.2615(5) | 37.1096(5) | 36.9621(5) | 37.4928(8) | 37.2553(14) | 37.3420(8) | 37.9940(7) |
| α [°]             | 90        | 90        | 90        | 90        | 90        | 90        | 90        | 90        | 90        |
| β [°]             | 90        | 90        | 90        | 90        | 90        | 90        | 90        | 90        | 90        |
| γ [°]             | 120       | 120       | 120       | 120       | 120       | 120       | 120       | 120       | 120       |
| V [Å³]            | 16832.0(10) | 16512.7(7) | 16748.9 | 16551.8(5) | 16461.4(5) | 17035.8(8) | 16751.8(13) | 16838.5(7) | 17706.2(8) |
| Z                  | 3.99996   | 3.99996   | 3.99996  | 3.99996  | 4         | 4         | 3.99996  | 4         | 3.99996  |
| ρcalc [g cm⁻³]    | 0.823     | 0.926     | 0.991     | 0.904     | 0.914     | 0.807     | 0.822     | 0.833     | 0.863     |
| µ [mm⁻¹]          | 2.470     | 2.610     | 3.651     | 2.529     | 2.558     | 2.939     | 3.314     | 0.63      | 2.897     |
| F (000)           | 4288.0    | 4672.0    | 5056.0    | 4672.0    | 4672.0    | 4256.0    | 4672.0    | 4360.0    | 4624.0    |
| Index ranges      | —20 ≤ h ≤ 23 | —20 ≤ s ≤ 23 | —28 ≤ h ≤ 28 | —28 ≤ h ≤ 28 | —27 ≤ h ≤ 25 | —23 ≤ s ≤ 22 | —22 ≤ s ≤ 22 | —28 ≤ s ≤ 22 | —16 ≤ s ≤ 29 |
| Refins collected  | 45568     | 60558     | 73594     | 69421     | 57708     | 44069     | 37180     | 133920    | 75940     |
| unique refins [Rint] | 8392(0.0657) | 10169(0.0766) | 11641(0.0902) | 11455(0.0952) | 11074(0.0742) | 6229(0.0538) | 6133(0.1182) | 11604(0.1270) | 12869(0.1057) |
| data/restraints/parameters | 8392/79/403 | 10169/122/447 | 11641/67/498 | 11455/48/511 | 11074/144/391 | 6229/0/409 | 6133/55/409 | 11604/62/409 | 12869/239/901 |
| GOF on F²         | 1.073     | 1.013     | 1.042     | 1.064     | 1.039     | 1.038     | 1.068     | 1.015     | 1.069     |
| R1, wR2 [I > 2σ(I)] | 0.0629, 0.1721 | 0.0809, 0.0202 | 0.0757, 0.1927 | 0.0736, 0.1900 | 0.0972, 0.2372 | 0.0576, 0.1595 | 0.1081, 0.2742 | 0.0542, 0.1246 | 0.0784, 0.2148 |
| R1, wR2 [all data] | 0.0927, 0.1912 | 0.1194, 0.2235 | 0.1088, 0.2153 | 0.0964, 0.2032 | 0.1467, 0.2771 | 0.0796, 0.1777 | 0.1938, 0.3396 | 0.0765, 0.1935 | 0.1087, 0.2431 |
| Δρmax/Δρmin (e Å⁻³) | 0.38/−0.28 | 0.76/−0.38 | 0.71/−0.37 | 0.84/−0.38 | 0.88/−0.29 | 0.25/−0.30 | 0.43/−0.57 | 0.32/−0.28 | 1.96/−1.70 |
| Flack parameter   | 0.048(11) | 0.150(11) | 0.034(7) | 0.056(6) | 0.104(14) | 0.007(7) | 0.006(13) | 0.118(12) | 0.409(6) |
| CCDC number       | 20561111 | 2056112 | 2056113 | 2056114 | 2056115 | 2056116 | 2056117 | 2056118 | 2056127 |
Table S5. BVS analysis for AlOC-99 to AlOC-120.

| AlOC-99 | AlOC-100 |
|---------|----------|
| A1 3.134 | Co1 1.854 | A1 3.113 | Co1 1.826 |
| A1-O1 1.896(2) | Co1-O1 1.956(4) | A1-O1 1.895(3) | Co1-O1 1.958(5) |
| A1-O1 1.896(2) | Co1-O3 2.054(3) | A1-O1 1.895(3) | Co1-O3 2.064(3) |
| A1-O1 1.896(2) | Co1-O3 2.054(3) | A1-O1 1.895(3) | Co1-O3 2.064(3) |
| A1-O2 1.886(3) | Co1-O3 2.054(3) | A1-O2 1.892(3) | Co1-O3 2.064(3) |
| A1-O2 1.886(3) | Co1-N1 2.184(6) | A1-O2 1.892(3) | Co1-N1 2.176(6) |
| A1-O2 1.886(3) | | A1-O2 1.892(3) | |

| AlOC-101 | AlOC-102 |
|----------|----------|
| A1 3.0159 | Co1 1.990 | A1 3.081 | Co1 1.977 |
| A1-O1 1.945(4) | Co1-O1 1.868(7) | A1-O1 1.898(6) | Co1-O1 1.893(10) |
| A1-O1 1.945(4) | Co1-O3 2.056(5) | A1-O1 1.898(6) | Co1-O2 2.047(8) |
| A1-O1 1.945(4) | Co1-O3 2.056(5) | A1-O1 1.898(6) | Co1-O2 2.047(8) |
| A1-O2 1.869(5) | Co1-O3 2.056(5) | A1-O3 1.896(7) | Co1-O2 2.047(8) |
| A1-O2 1.869(5) | Co1-N1 2.170(11) | A1-O3 1.896(7) | Co1-N1 2.250(14) |
| A1-O2 1.869(5) | | A1-O3 1.896(7) | |

| AlOC-103 | AlOC-104 |
|----------|----------|
| A1 3.081 | Co1 1.856 | A1 3.157 | Co1 1.918 |
| A1-O1 1.891(5) | Co1-O2 1.942(8) | A1-O1 1.882(6) | Co1-O1 1.970(10) |
| A1-O1 1.891(5) | Co1-O3 2.081(5) | A1-O1 1.882(6) | Co1-O3 2.032(7) |
| A1-O1 1.891(5) | Co1-O3 2.081(5) | A1-O1 1.882(6) | Co1-O3 2.032(7) |
| A1-O2 1.892(5) | Co1-O3 2.081(5) | A1-O2 1.894(7) | Co1-O3 2.032(7) |
| A1-O2 1.892(5) | Co1-N1 2.096(10) | A1-O2 1.894(7) | Co1-N1 2.213(13) |
| A1-O2 1.892(5) | | A1-O2 1.894(7) | |

| AlOC-105 | AlOC-106 |
|----------|----------|
| A1 3.081 | Co1 1.880 | A1 3.157 | Mn1 1.934 |
| A1-O1 1.894(6) | Co1-O2 1.963(10) | A1-O1 1.889(2) | Mn1-O1 2.029(4) |
| A1-O1 1.894(6) | Co1-O3 2.041(7) | A1-O1 1.889(2) | Mn1-O3 2.132(4) |
| A1-O1 1.894(6) | Co1-O3 2.041(7) | A1-O1 1.889(2) | Mn1-O3 2.132(4) |
| A1-O2 1.890(6) | Co1-O3 2.041(7) | A1-O2 1.899(3) | Mn1-O3 2.123(4) |
| A1-O2 1.890(6) | Co1-N1 2.192(14) | A1-O2 1.899(3) | Mn1-N1 2.256(7) |
| A1-O2 1.890(6) | | A1-O2 1.899(3) | |

| AlOC-107 | AlOC-108 |
|----------|----------|
| A1 3.147 | Fe1 2.006 | A1 3.129 | Zn1 1.939 |
| A1-O1 1.890(2) | Fe1-O1 1.990(4) | A1-O1 1.897(16) | Zn1-O2 1.960(3) |
| A1-O1 1.890(2) | Fe1-O3 2.077(3) | A1-O1 1.897(16) | Zn1-O3 2.059(2) |
| A1-O1 1.890(2) | Fe1-O3 2.077(3) | A1-O1 1.897(16) | Zn1-O3 2.059(2) |
| A1-O2 1.889(3) | Fe1-O3 2.077(3) | A1-O2 1.886(19) | Zn1-O3 2.059(2) |
| A1-O2 1.889(3) | Fe1-N1 2.190(5) | A1-O2 1.886(19) | Zn1-N1 2.178(4) |
| A1-O2 1.889(3) | | A1-O2 1.886(19) | |

| AlOC-109 | AlOC-110 |
|----------|----------|
| A1 3.130 | Co1 1.845 | A1 3.168 | Fe1 2.009 |
| A1-O1 1.896(3) | Co1-O1 1.959(5) | A1-O1 1.885(3) | Fe1-O1 1.977(5) |
| A1-O1 1.896(3) | Co1-O3 2.058(5) | A1-O1 1.885(3) | Fe1-O3 2.088(4) |
| A1-O1 1.896(3) | Co1-O3 2.058(5) | A1-O1 1.885(3) | Fe1-O3 2.088(4) |
| A1-O2 1.887(4) | Co1-O3 2.058(5) | A1-O2 1.889(4) | Fe1-O3 2.088(4) |
| A1-O2 1.887(4) | Co1-N1 2.172(7) | A1-O2 1.889(4) | Fe1-N1 2.167(7) |
| A1-O2 1.887(4) | | A1-O2 1.889(4) | |
| AlOC-111 |  |
|----------|----------|
| Al1 3.070 | Cd1 2.142 |
| Al1—O1 1.896(4) | Cd1—O1 2.075(7) |
| Al1—O1 1.896(4) | Cd1—O3 2.294(5) |
| Al1—O1 1.896(4) | Cd1—O3 2.294(5) |
| Al1—O2 1.901(4) | Cd1—O3 2.294(5) |
| Al1—O2 1.901(4) | Cd1—N1 2.239(9) |
| Al1—O2 1.901(4) | Cd1—N1 2.239(9) |

| AlOC-112 |  |
|----------|----------|
| Al1 3.168 | Al2 3.168 |
| Al1—O1 1.902(4) | Al2—O1 1.910(5) |
| Al1—O1 1.902(4) | Al2—O1 1.910(5) |
| Al1—O1 1.902(4) | Al2—O3 1.888(6) |
| Al1—O2 1.897(4) | Al2—O4 1.884(5) |
| Al1—O2 1.898(4) | Al2—O5 1.900(4) |
| Al1—O2 1.897(5) | Al2—O8 1.890(5) |

| AlOC-113 |  |
|----------|----------|
| Al1 3.200 | Al2 3.035 |
| Al1—O1 1.886(5) | Al2—O1 1.885(6) |
| Al1—O1 1.886(5) | Al2—O1 1.910(5) |
| Al1—O1 1.886(5) | Al2—O3 1.891(4) |
| Al1—O9 1.880(6) | Al2—O4 1.906(6) |
| Al1—O9 1.880(6) | Al2—O5 1.917(5) |
| Al1—O9 1.880(6) | Al2—O6 1.908(5) |

| AlOC-114 |  |
|----------|----------|
| Al1 3.109 | Al2 3.141 |
| Al1—O1 1.888(5) | Al2—O2 1.894(4) |
| Al1—O2 1.886(5) | Al2—O2 1.894(4) |
| Al1—O2 1.914(5) | Al2—O2 1.894(4) |
| Al1—O3 1.888(4) | Al2—O5 1.886(5) |
| Al1—O4 1.895(6) | Al2—O5 1.886(5) |
| Al1—O8 1.892(6) | Al2—O5 1.886(5) |

| AlOC-115 |  |
|----------|----------|
| Al1 3.104 | Al2 3.077 |
| Al1—O1 1.894(4) | Al2—O1 1.903(5) |
| Al1—O2 1.894(4) | Al2—O1 1.899(5) |
| Al1—O2 1.894(4) | Al2—O2 1.895(3) |
| Al1—O3 1.895(4) | Al2—O5 1.897(5) |
| Al1—O4 1.895(4) | Al2—O6 1.896(4) |
| Al1—O8 1.895(4) | Al2—O8 1.896(5) |

| AlOC-116 |  |
|----------|----------|
| Al1 3.078 | Al2 3.160 |
| Al1—O1 1.904(5) | Al2—O1 1.895(6) |
| Al1—O1 1.904(5) | Al2—O1 1.886(6) |
| Al1—O1 1.904(5) | Al2—O2 1.874(6) |
| Al1—O4 1.891(5) | Al2—O3 1.905(5) |
| Al1—O4 1.891(5) | Al2—O5 1.894(6) |
| Al1—O4 1.891(5) | Al2—O7 1.873(7) |

| AlOC-117 |  |
|----------|----------|
| AlOC-111 |  |
| AlOC-112 |  |
| AlOC-113 |  |
| AlOC-114 |  |
| AlOC-115 |  |
| AlOC-116 |  |

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| Distances |  | Distances |  | Distances |  | Distances |  |
|-----------|---|-----------|---|-----------|---|-----------|---|
| A1  3.153 | A1  3.114 | Mn1  2.028 | Mn1―O4  2.004(8) | Mn2  2.015 | Mn2―O1  1.997(5) | Mn2―O7  2.133(7) |
| A1―O1  1.887(5) | A12―O1  1.888(6) | Mn1―O9  2.130(6) | Mn2―O8  2.132(7) | Mn2―N2  2.196(6) |
| A1―O1  1.887(5) | A12―O1  1.902(6) | Mn1―O9  2.130(6) | Mn2―O8  2.132(7) | Mn2―N2  2.196(6) |
| A1―O1  1.887(5) | A12―O3  1.915(6) | Mn1―O9  2.130(6) | Mn2―O8  2.132(7) | Mn2―N2  2.196(6) |
| A1―O2  1.890(6) | A12―O4  1.893(4) | Mn1―N1  2.200(11) | Mn2―N2  2.196(6) |
| A1―O2  1.890(6) | A12―O5  1.880(5) | Mn1―N1  2.200(11) | Mn2―N2  2.196(6) |
| A1―O2  1.890(6) | A12―O6  1.882(6) | Mn1―N1  2.200(11) | Mn2―N2  2.196(6) |

| Distances |  | Distances |  | Distances |  | Distances |  |
|-----------|---|-----------|---|-----------|---|-----------|---|
| A1OC-118  | A1  3.088 | A12  3.064 | Fe1  1.919 | Fe1―O4  2.02(2) | Fe2  2.231 | Fe2―O1  1.958(10) | Fe2―O7  2.057(16) |
| A1―O1  1.936(12) | A12―O1  1.876(13) | Fe1―O9  2.094(13) | Fe2―O8  2.036(15) |
| A1―O1  1.936(12) | A12―O1  1.896(14) | Fe1―O9  2.094(13) | Fe2―O8  2.036(15) |
| A1―O1  1.936(12) | A12―O2  1.922(16) | Fe1―O9  2.094(13) | Fe2―O8  2.036(15) |
| A1―O3  1.861(13) | A12―O4  1.878(11) | Fe1―O9  2.094(13) | Fe2―O8  2.036(15) |
| A1―O3  1.861(13) | A12―O5  1.924(14) | Fe1―N1  2.18(3) | Fe2―N2  2.128(14) |
| A1―O3  1.861(13) | A12―O6  1.904(11) | Fe1―N1  2.18(3) | Fe2―N2  2.128(14) |

| Distances |  | Distances |  | Distances |  | Distances |  |
|-----------|---|-----------|---|-----------|---|-----------|---|
| A1OC-119  | A1  3.014 | A12  3.066 | Zn1  1.828 | Zn1―O6  1.991(5) | Zn2  1.880 | Zn2―O1  1.967(3) | Zn2―O7  2.081(4) |
| A1―O1  1.897(3) | A12―O1  1.900(4) | Zn1―O4  2.079(4) | Zn2―O9  2.075(4) |
| A1―O1  1.897(3) | A12―O2  1.899(4) | Zn1―O4  2.079(4) | Zn2―O9  2.075(4) |
| A1―O1  1.897(3) | A12―O2  1.912(4) | Zn1―O4  2.079(4) | Zn2―O9  2.075(4) |
| A1―O3  1.914(3) | A12―O4  1.903(3) | Zn1―O4  2.079(4) | Zn2―O9  2.075(4) |
| A1―O3  1.914(3) | A12―O5  1.889(3) | Zn1―N2  2.189(6) | Zn2―N1  2.166(4) |
| A1―O3  1.914(3) | A12―O6  1.892(4) | Zn1―N2  2.189(6) | Zn2―N1  2.166(4) |

| Distances |  | Distances |  | Distances |  | Distances |  |
|-----------|---|-----------|---|-----------|---|-----------|---|
| A1OC-120  | A1  3.119 | A12  2.978 | Cd1  2.206 | Cd1―O5  2.057(9) | Cd2  2.211 | Cd2―O2  2.084(5) |
| A1―O2  1.887(6) | A12―O1  1.901(8) | Cd1―O7  2.279(8) | Cd2―O8  2.284(8) |
| A1―O2  1.887(6) | A12―O2  1.894(8) | Cd1―O7  2.279(8) | Cd2―O8  2.284(8) |
| A1―O2  1.887(6) | A12―O2  1.890(8) | Cd1―O7  2.279(8) | Cd2―O8  2.284(8) |
| A1―O3  1.898(6) | A12―O4  1.907(7) | Cd1―O7  2.279(8) | Cd2―O8  2.284(8) |
| A1―O3  1.898(6) | A12―O5  1.904(5) | Cd1―N2  2.247(12) | Cd2―N1  2.226(7) |
| A1―O3  1.898(6) | A12―O6  1.966(7) | Cd1―N2  2.247(12) | Cd2―N1  2.226(7) |
Table S6. Direct aldol reactions catalyzed by AlOCs.\textsuperscript{[a]}

\textbf{Entry} & \textbf{catalyst} & \textbf{yield/} % \\
\hline
1 & AlOC-99 (10 mol\%) & 79\% \textsuperscript{[b]} \\
2 & AlOC-109 (10 mol\%) & 87\% \textsuperscript{[b]} (88\% \textsuperscript{[c]}) \\
3 & AlOC-112 (10 mol\%) & 88\% \textsuperscript{[b]} \\
4 & AlOC-99 (5 mol\%) & 48\% \textsuperscript{[b]} \\
5 & AlOC-109 (5 mol\%) & 67\% \textsuperscript{[b]} \\
6 & AlOC-112 (5 mol\%) & 68\% \textsuperscript{[b]} \\
7 & Without Catalyst & none \\

\textsuperscript{[a]} Firstly, the mixed solution of catalyst, acetone (0.2 mL) and DMSO (0.8 mL) was stirred at room temperature for 15 min. Then, 4-nitrobenzaldehyde (0.1 mmol) was added and the solution further stirred at 60 °C for 48 h. \textsuperscript{[b]} The yield of the isolated product based on 4-nitrobenzaldehyde. \textsuperscript{[c]} The yield of isolated product based on 4-nitrobenzaldehyde after three runs.

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