Electronic Supplementary Material (ESI) for Dalton Transactions.

Hydroxamate based transition metal-organic coordination polymers with semiconductive properties

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Table S1 Single crystal structure data of **Mn-ONDI-1**, **CdCl-ONDI**, **Mn-ONDI-2**.

	Mn-ONDI-1	**Mn-ONDI-2**	**CdCl-ONDI**
Empirical formula	$C_{14}H_8N_2O_8Mn$	$C_{14}H_6N_2O_7Mn{\cdot}H_2O$	$C_{14}H_4N_2O_6Cd_2Cl_2$
Formula weight/g·mol^{-1}	387.16	387.16	591.89
Temperature/K	180	180	180
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*C2/c*
a, Å	6.9888(2)	7.0493(3)	20.7322(13)
b, Å	8.4994(3)	9.1088(4)	3.8637(2)
c, Å	11.9404(4)	11.3580(4)	20.6366(14)
α (deg)	70.725(2)	76.213(3)	90
β (deg)	74.189(2)	80.550(3)	110.650(5)
γ (deg)	70.343(2)	68.314(3)	90
V/Å^3	620.01(4)	655.82(5)	1546.85(17)
Z	2	2	4
λ/Å	1.54186	1.54186	1.54186
D_{calc}(g cm-3)	2.074	1.961	2.542
μ/mm^{-1}	9.239	8.735	25.577
F(000)	390	390	1120
Reflections collected	11574	12606	5479
Independent reflections	2314 (R_{int} = 0.0482)	2474 (R_{int} = 0.0296)	1455 (R_{int} = 0.0343)
Observed refl. [I > 2σ(I)]	2150	2277	1229
Completeness	0.986(θ=70.583)	0.993 (θ = 70.835)	0.986 (θ = 70.358)
GOF	1.040	1.063	1.077
R1[a], wR_2[b] [I > 2σ(I)]	0.0440, 0.1203	0.0320, 0.0883	0.0718, 0.1947
R_1[a], wR_2[b] (all data)	0.0474, 0.1247	0.0356, 0.0924	0.0821, 0.2062
CCDC number	2167220	2167221	2167222
a) $R1 = \Sigma\|\|F_o\|-\|F_c\|\| / \Sigma\|F_o\|$; b) $wR_2 = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$			

Table S2 Bond lengths of carbonyl groups (C=O) in **Mn-ONDI-1** and **CdCl-ONDI**.

Item	**C=O (coordinated)**	**C=O (free)**
Mn-ONDI-1	1.245 (3) Å	1.210 (3) Å 1.224(4) Å 1.214(4) Å
CdCl-ONDI	1.19(2) Å 1.17(2) Å	N/A

Table S3 π–π interactions and interplanar distances, and electrical conductivity of H_2ONDI based coordination polymers.

Item	Shortest π–π interactions distance (centroid-centroid)	Interplanar distance	Electrical conductivity (pressed pellets)
H_2ONDI·DMA[8]	3.607 Å	3.410 Å	2.26×10^{-7} S/m
$[Ca(ONDI)(H_2O)_2]_\infty$[8]	3.179 Å	N/A	1.03×10^{-5} S/m
$[Sr(ONDI)(H_2O)_2]_\infty$[8]	3.249 Å	N/A	2.21×10^{-5} S/m
$[Mn(ONDI)(H_2O)_2]_\infty$ (This work)	3.433 Å	3.267 Å	3.7×10^{-6} S/m
$[Cd_2Cl_2(ONDI)]_\infty$ (This work)	3.569 Å	3.487 Å	3.5×10^{-7} S/m

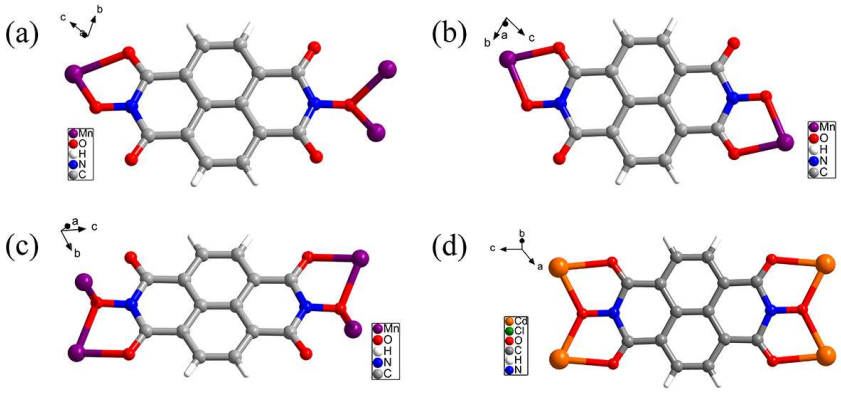

Fig. S1 Coordination modes of $ONDI^{2-}$ in **Mn-ONDI-1** (a), in **Mn-ONDI-2** (b) and (c), in **CdCl-ONDI** (d).

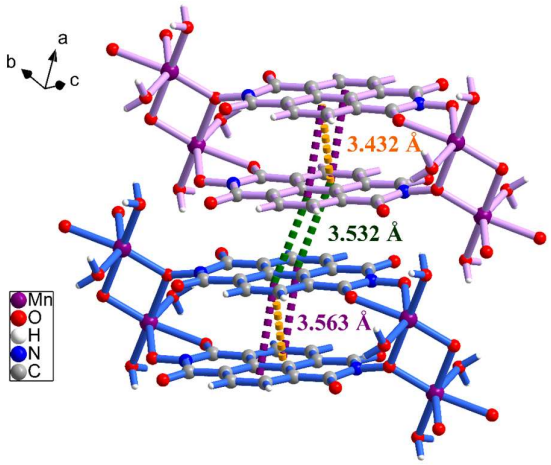

Fig. S2 π–π interactions in **Mn-ONDI-1**; same colour as in **Fig. 2**; dashed lines represent equivalent centroid–centroid distances.

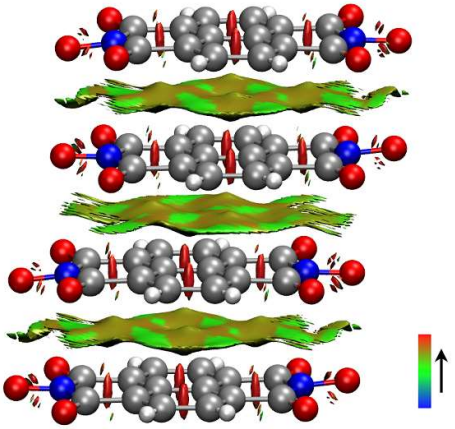

Fig. S3 Gradient isosurfaces (s = 0.5 a.u.) for a fragment of **Mn-ONDI-1**. The surfaces are colored on a blue-green-red (BGR) scale according to values of sign(λ_2)ρ, ranging from –0.04 to 0.02 a.u.. Blue indicates strong attractive interactions, and red indicates strong non-bonded overlap.

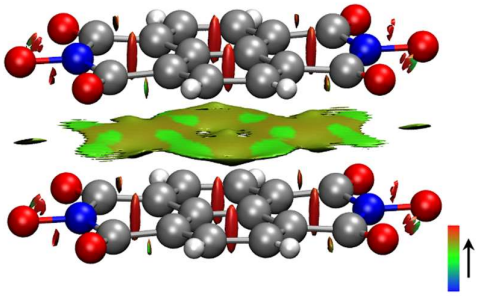

Fig. S4 Gradient isosurfaces (s = 0.5 a.u.) for a fragment of **CdCl-ONDI**. The surfaces are colored on a blue-green-red (BGR) scale according to values of sign(λ_2)ρ, ranging from –0.04 to 0.02 a.u.. Blue indicates strong attractive interactions, and red indicates strong non-bonded overlap.

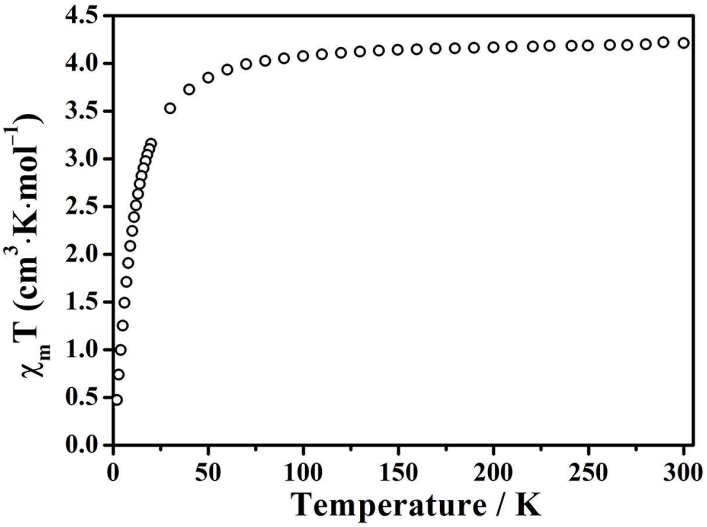

Fig. S5 Temperature dependent magnetic susceptibility of **Mn-ONDI-1**.

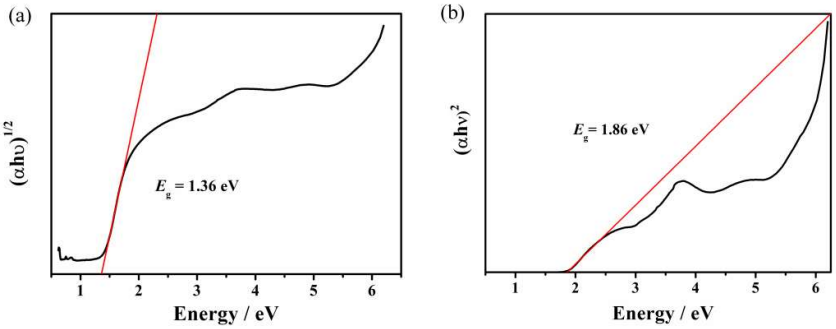

Fig. S6 Tauc plots of **Mn-ONDI-1** (a) and **CdCl-ONDI** (b).

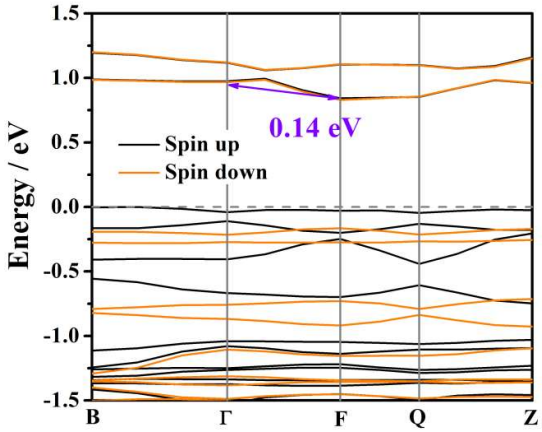

Fig. S7 Band structure of **Mn-ONDI-1** marked with dispersion width value.

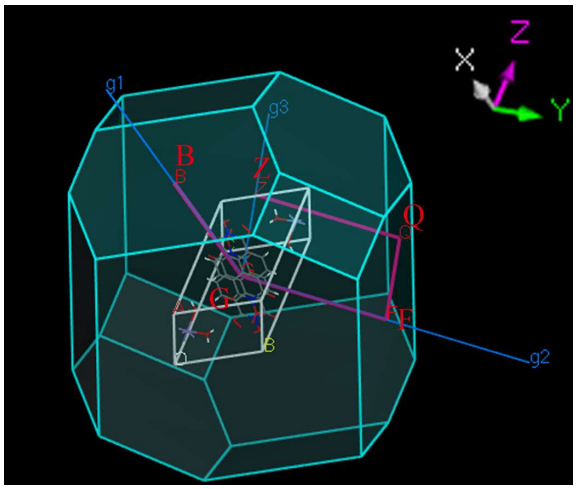

Fig. S8 K-point path in Brillouin zone of **Mn-ONDI-1** (Γ is denoted as G).

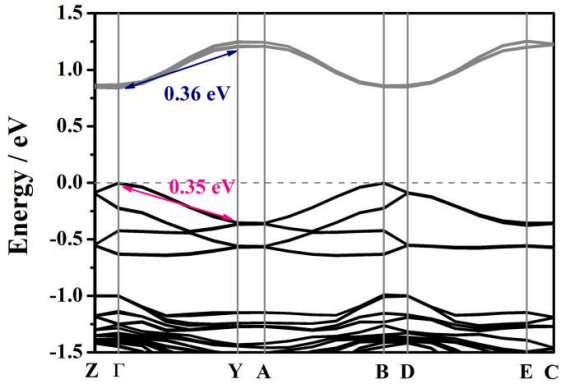

Fig. S9 Band structure of **CdCl-ONDI** marked with dispersion width value.

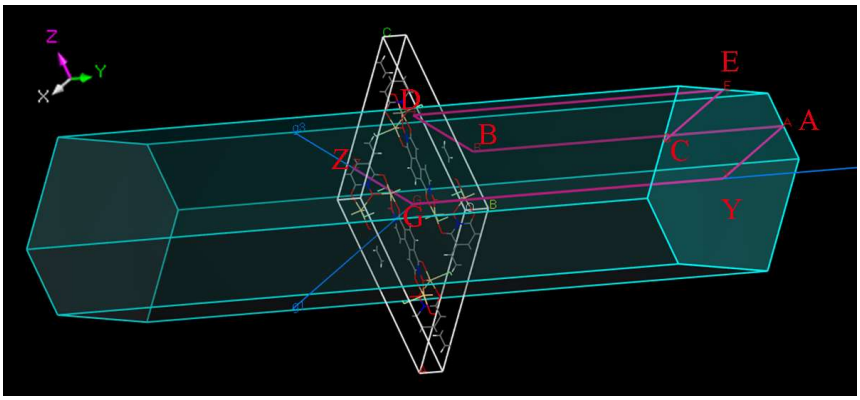

Fig. S10 K-point path in Brillouin zone of **CdCl-ONDI** (Γ is denoted as G).

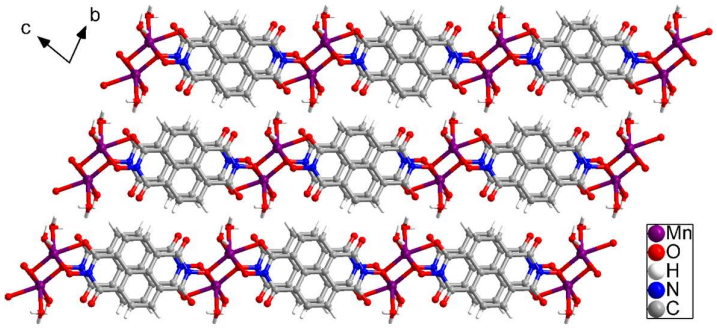

Fig. S11 A prospective of the coordination chains arrangement of **Mn-ONDI-1**, view along the *a* axis.

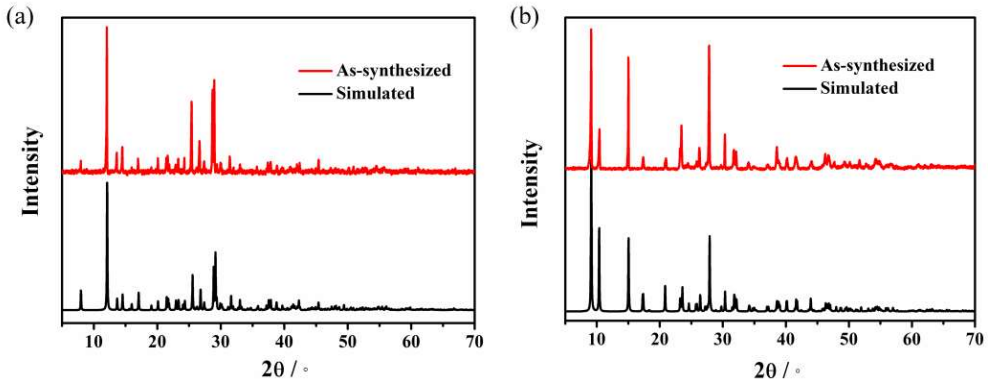

Fig. S12 PXRD patterns of **Mn-ONDI-1** (a) and **CdCl-ONDI** (b); λ(Cu-$K_{\alpha 1}$) = 1.54060 Å.

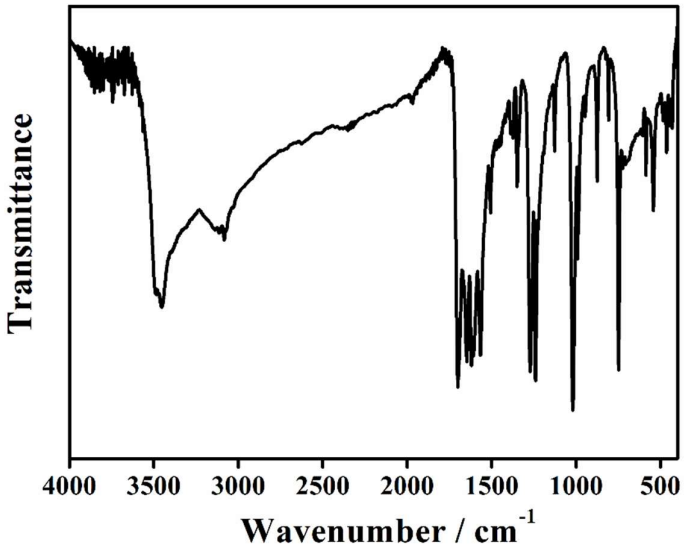

Fig. S13 IR spectrum of **Mn-ONDI-1**.

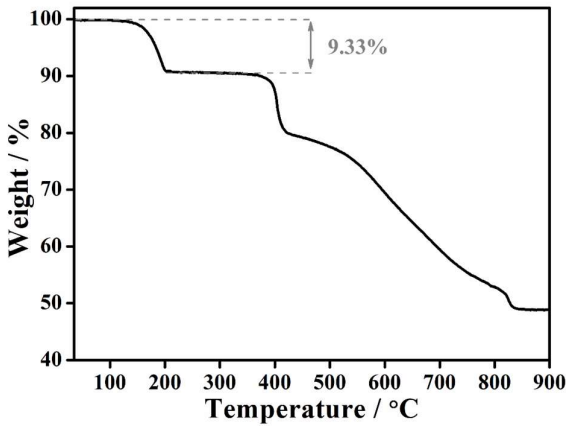

Fig. S14 TG curve of **Mn-ONDI-1**. The weight loss of 9.33% at 150-200 °C corresponds to the loss of coordinated H_2O molecules (calculated weight loss 9.30%).

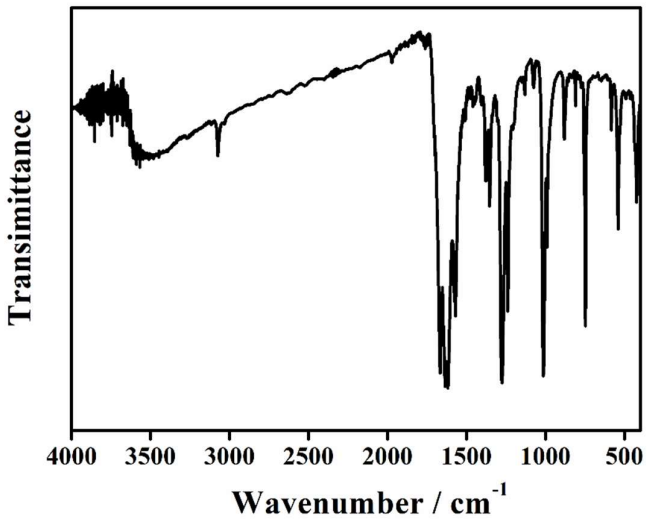

Fig. S15 IR spectrum of **CdCl-ONDI**.

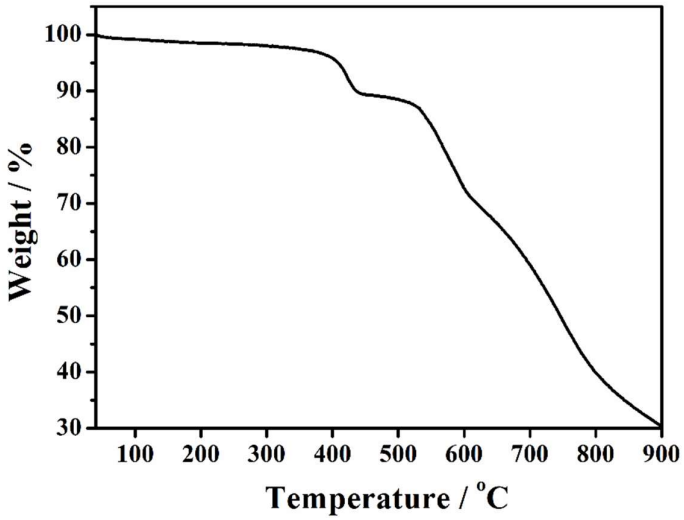

Fig. S16 TG curve of **CdCl-ONDI**.

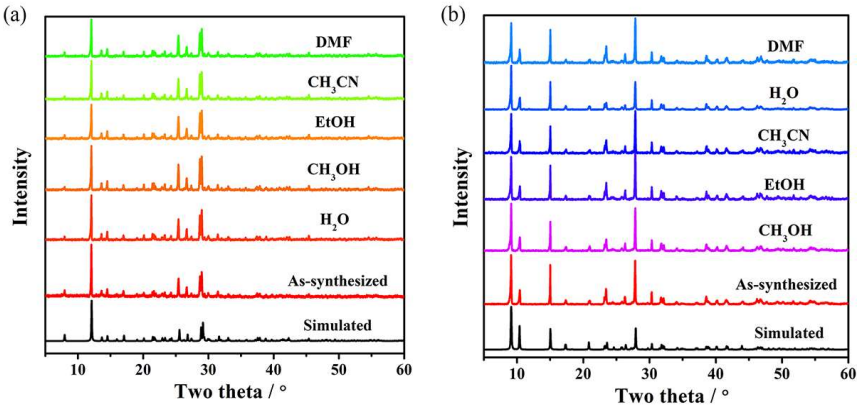

Fig. S17 PXRD patterns of **Mn-ONDI-1** (a) and **CdCl-ONDI** (b) after immersion in different solvents for 3 days. From their PXRD patterns, **Mn-ONDI-1** and **CdCl-ONDI** both exhibited high stability in common solvents, which could be assigned to strong metal-hydroxamate bonds.[1]

Reference:

1. J. A. Chiong, J. Zhu, J. B. Bailey, M. Kalaj, R. H. Subramanian, W. Xu, S. M. Cohen and F. Akif Tezcan, *J. Am. Chem. Soc.*, 2020, **142**, 6907−6912.