# Semiconductive Coordination Polymers with continuous $\pi-\pi$ interactions and defined crystal structures

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## 1. Experimental section

## **1.1 Materials and Instruments**

All reagents were purchased commercially and used without further purification. Elemental analyses were carried out on a VARIO EL analyzer (Elementar). Thermogravimetric (TG) analyses were recorded in Al<sub>2</sub>O<sub>3</sub> crucibles on a NETZSCH STA 449 F1 thermal analyzer under N<sub>2</sub> (25 ml·min<sup>-1</sup>) atmosphere at a heating rate of 10 K·min<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns were collected on a STOE STADI-P diffractometer using Cu-K<sub>a1</sub> radiation ( $\lambda = 154.060$  pm) at room temperature in the 20 range of 5-80°. UV-Vis absorption spectra were collected on a Jasco V-670 UV–Vis–NIR spectrometer. IR spectra were measured on a Bruker TENSOR 27 spectrometer. The electron paramagnetic resonance (EPR) measurements were recorded on a Bruker EMX X-band micro spectrometer at room temperature.

# 1.2 Synthesis of [Ca(ONDI)(H<sub>2</sub>O)<sub>2</sub>]<sub>∞</sub> (Ca-ONDI) and [Sr(ONDI)(H<sub>2</sub>O)<sub>2</sub>]<sub>∞</sub> (Sr-ONDI)

2,7-dihydroxybenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (H<sub>2</sub>ONDI) was synthesized based on a reported method<sup>1</sup> and used directly for synthesis of coordination polymer without any further purification.

Crystals of H<sub>2</sub>ONDI·DMA were obtained by recrystallization from a solvent mixture of DMA and CH<sub>3</sub>CN and used to measure UV-vis absorption, cyclic voltammetry, and electrical conductivity.

**Ca-ONDI**: A mixture containing H<sub>2</sub>ONDI (15 mg, 0.05 mmol) and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (9 mg, 0.04 mmol) in 1.5 mL DMF and 3 mL H<sub>2</sub>O was sealed in a Teflon lined autoclave and heated under autogenous pressure at 100 °C for 3 days, and then allowed to cool down to room temperature in 9 hours. Brown crystals were isolated. Microcrystalline **Ca-ONDI** was obtained by heating a mixture of H<sub>2</sub>ONDI (300 mg, 1 mmol) and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (236 mg, 1 mmol) in 30 mL DMF and 15 mL H<sub>2</sub>O under reflux for 3 days. The resulting brown microcrystalline powder was filtered off. After

washing with DMSO and CH<sub>3</sub>OH several times, the product was collected in 40% yield. Anal. Calc. (%) for CaC<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>8</sub> (M=372.30 g/mol): C, 45.16; H, 2.16; N, 7.52. Found (%): C, 45.39; H, 1.89; N, 7.75. IR (KBr pellet, cm<sup>-1</sup>): 3473 m, 3408 m, 3229 m, 3070 m, 1978 w, 1701 s, 1684 s, 1571 s, 1509 w, 1382 w, 1270 s, 1242 s, 1130 w, 1023 s, 986 m, 877 m, 751 s, 585 m, 534 m, 461 w.

**Sr-ONDI**: Single crystals and a microcrystalline sample of Sr-ONDI were synthesized in the same way as **Ca-ONDI** except the metal salt was replaced by anhydrous  $Sr(NO_3)_2$  and the solvent DMF was replaced by DMA. Anal. Calc. (%): C, 39.93; H, 1.92; N, 6.65. Found (%): C, 40.08; H, 1.73; N, 6.56. IR (KBr pellet, cm<sup>-1</sup>): 3528 m, 3384 m, 3229 m, 3070 m, 1978 w, 1701 s, 1684 s, 1571 s, 1509 w, 1382 w, 1270 s, 1242 s, 1130 w, 1023 s, 986 m, 877 m, 751 s, 585 m, 534 m, 461 w. (Me<sub>2</sub>NH<sub>2</sub>)(HONDI): A suspension of H<sub>2</sub>ONDI (15 mg, 0.05 mmol) in DMF (2 mL) and CH<sub>3</sub>OH (2 mL) was sealed in a Teflon lined autoclave and heated under autogenous pressure at 80 °C for 3 days, and then allowed to cool down to room temperature within 3 h. Brown crystals were obtained. After washing with CH<sub>3</sub>OH several times, the product was collected with about 50% yield. Anal. Calc. (%) for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>6</sub> (M=343.30 g/mol): C, 55.93; H, 3.79; N, 12.23. Found (%): C, 56.11; H, 3.43; N, 12.38. IR (KBr pellet, cm<sup>-1</sup>): 3323 w, 2976 s, 2784 s, 2475 s, 1945 m, 1712 s, 1674 s, 1641 s, 1609 s, 1575 s, 1470 m, 1420 w, 1407 w, 1392 w, 1365 m,1332 s, 1255 s, 1244 s, 1227 s, 1207 s, 1118 m, 1023 m, 1001 s, 986 s, 978 s, 892 m, 878 s, 750 s, 733 s, 575 s, 526 m, 517 m, 481 w, 442 m, 433 m.

#### 1.3 X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a STOE STADIVARI, equipped with an X-ray micro-source (Cu-K $\alpha$ ,  $\lambda = 154.186$  pm) and a DECTRIS Pilatus 300k detector. Due to twinning of **Sr-ONDI**, (Me<sub>2</sub>NH<sub>2</sub>)(HONDI), and H<sub>2</sub>ONDI·DMA crystals, their data sets were processed with the program STOE X-AREA<sup>2</sup> to generate *hklf5* files for further crystal structure determination. The structures were solved by direct methods and refined using SHELX.<sup>3</sup> The hydrogen atoms of the ligands were added geometrically and treated using the riding model. The final structures were refined using a full-matrix least-squares refinement on  $F^2$ . All calculations were performed using the Olex2 crystallographic software.<sup>4</sup>

CCDC 2090235-2090237 and 2106731 contain the supplementary crystallographic data for (Me<sub>2</sub>NH<sub>2</sub>)(HONDI), Ca-ONDI, Sr-ONDI and H<sub>2</sub>ONDI·DMA. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, by emailing to data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

Empirical formula	C14H8CaN2O8	$C_{14}H_8N_2O_8Sr$	C16H13N3O6	C18H15N3O7
	(Ca-ONDI)	(Sr-ONDI)	(Me2NH2)(HONDI)	(H <sub>2</sub> ONDI·DMA)
Formula	372.30	419.84	343.30	385.33
weight/g·mol <sup>-1</sup>				
Temperature/K	180	180	180	295
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_{1}/n$	$P2_1/n$	PĪ	PĪ
<i>a,</i> Å	12.1377(13)	12.2948(8)	6.6813(7)	7.4711(3)
<i>b,</i> Å	6.4120(5)	6.5450(3)	9.1526(9)	8.7536(4)
<i>c,</i> Å	16.7906(16)	16.9823(9)	12.8079(13)	14.0801(7)
a (deg)	90	90	71.835(8)	78.791(4)
β (deg)	105.110(8)	104.890(5)	78.233(9)	82.589(4)
γ (deg)	90	90	71.616(8)	67.238(3)
V/Å <sup>3</sup>	1261.6(2)	1320.67(13)	701.34(13)	831.44(7)
Ζ	4	4	2	2
λ/Å	1.54186	1.54186	1.54186	1.54186
$D_{\text{calc}}(\text{g cm-3})$	1.960	2.112	1.626	1.539
$\mu/\text{mm}^{-1}$	4.864	6.222	1.081	1.028
F(000)	760	832	356	400.0
Reflections	12344	20273	20194	26543
collected				
Independent	$2394 (R_{int} = 0.0405)$	$4396 (R_{int} = 0.0759)$	$4632 (R_{\rm int}{=}0.0563)$	5795 (R <sub>int</sub> =
reflections				0.0405)
Observed refl.	1990	3313	3092	2912
$[I > 2\sigma(I)]$				
Completeness	0.991(θ=70.577)	$1.000 \ (\theta = 68.000)$	$0.995 (\theta = 67.983)$	0.998(θ=70.885)
Twin domains	N/A	0.598(2) / 0.402(2)	0.623(2) / 0.377(2)	0.726(2)/0.274(2)
GOF	1.083	1.071	1.021	0.968
R1 <sup>a</sup> , wR2 <sup>b</sup> [I >	0.0344, 0.0895	0.0548, 0.1498	0.0600, 0.1456	0.0803, 0.2375
2σ(I)]				
R1 <sup>a</sup> , wR2 <sup>b</sup> (all data)	0.0441, 0.0951	0.0667, 0.1594	0.0870, 0.1575	0.1182, 0.2652
residual diff.	0.52 / -0.47	0.61/0.83	0.26/-0.31	0.67/ -0.37
density max. / min.				
CCDC number	2090235	2090236	2090237	2106731
a) R1 = $\Sigma   F_o  -  F_c   / \Sigma  F_o ;$ b) wR <sub>2</sub> = $[\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$				

Table S1 Single crystal structure data of Ca-ONDI, Sr-ONDI,  $(Me_2NH_2)(HONDI)$ , and  $H_2ODNI \cdot DMA$ .

#### 1.4 Cyclic voltammetry

The solid-state cyclic voltammograms of **Ca-ONDI** and **Sr-ONDI** were measured using a threeelectrode cell at room temperature. About 8 mg of **Ca-ONDI** or **Sr-ONDI** powder were dispersed in a solution of 1 mL ethanol, 1 mL H<sub>2</sub>O, and 40  $\mu$ L of a 5% w/w Nafion solution in water and 1propanol for 5 min. A 20  $\mu$ l aliquot of the above dispersion was drop-cast onto the working electrode, a precleaned glassy carbon electrode, and dried in air. A Pt wire and a Ag/Ag<sup>+</sup> electrode acted as the counter and the reference electrode, respectively. Electrochemical measurements were carried out in 0.1M [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub> solution in acetonitrile under N<sub>2</sub> atmosphere. The reduction potentials of the **Ca-ONDI** and **Sr-ONDI** were obtained from the cyclic voltammogram and referenced with respect to Fc/Fc<sup>+</sup> as internal standard.

The cyclic voltammogram of H<sub>2</sub>ONDI was measured in 0.1M [(n-Bu)<sub>4</sub>N]PF<sub>6</sub> solution in DMA under N<sub>2</sub> atmosphere. The concentration of H<sub>2</sub>ONDI was about  $5 \times 10^{-3}$  mmol/mL. Ferrocene was used as internal standard.

#### 1.5 Electrical conductivity measurements

Pellets (diameter 13 mm, thickness ca. 0.7 mm) of **Ca-ONDI** and **Sr-ONDI** were prepared using press dies. The conductivity of these pellets was measured on a Biologic SP-150 potentiostat. The direct current-voltage (I-V) curves of **Ca-ONDI** and **Sr-ONDI** pellets sandwiched between two silver gel coated hard plastic sheets covered with Cu film as electrodes were recorded under ambient conditions from -1 to +1 V. The specific electric conductivity  $\sigma$  was calculated by  $\sigma = \frac{1}{V} \cdot \frac{l}{\pi r^2}$ , where *l* is the thickness, r is the radius of the pellet.

#### **1.6 Computational details**

1) Calculation of intermolecular interactions in **Ca-ONDI** and **Sr-ONDI**: The plots of the electron density ( $\rho$ ) and reduced density gradient (s =  $1/(2(3\pi^2)^{1/3})|\nabla\rho|/\rho^{4/3}$ ) were obtained by density functional theory calculations.<sup>5</sup> Calculations were performed with the B3LYP functional and the 6-311G (d,p) basis set,<sup>6</sup> using the Gaussian 09 program.<sup>7</sup> The results were analyzed by Multiwfn.<sup>8</sup> 2) The band structure, DOS and linear optical properties were calculated using the CASTEP package.<sup>9</sup> The structural models for **Ca-ONDI** and **Sr-ONDI** were built directly from the singlecrystal X-ray diffraction data. The exchange-correlation energy was described by the PBE functional within the GGA.<sup>10, 11</sup> The norm conserving pseudopotentials were chosen to modulate the electron-ion interaction.<sup>12, 13</sup> The plane-wave cutoff energy was 750 eV, and the threshold of 5×10<sup>-7</sup> eV was set for the self-consistent field convergence of the total energy. The Fermi level was selected as the reference and set to 0 eV by default. Other parameters were set to default values.

# 2. Figures



**Fig. S1** PXRD patterns of **Ca-ONDI** (a) and **Sr-ONDI** (b) in red and the corresponding simulated diffraction patterns based on single crystal data (black).



Fig. S2 IR spectra of Ca-ONDI (red) and Sr-ONDI (black).



**Fig. S3** TG curves of **Ca-ONDI** and **Sr-ONDI**. The weight loss of 9.88% (**Ca-ONDI**) and 8.56% (**Sr-ONDI**) at 150-250 °C correspond to the loss of coordinating H<sub>2</sub>O molecules (calculated weight loss 9.67% and 8.57% for **Ca-ONDI** and **Sr-ONDI**, respectively).



**Fig. S4** Intermolecular  $\pi$ - $\pi$  interactions in **Sr-ONDI**. Symmetry codes: A, 0.5-x, 0.5+y, 0.5-z; D, 0.5-x, -0.5+y, 0.5-z. Plane 1 and plane 2 refer to the planes containing Cg1A and Cg2A and the plane containing Cg1D and Cg2D, respectively. Cg3: C5 $\rightarrow$ C4 $\rightarrow$ C3 $\rightarrow$ C2 $\rightarrow$ C13 $\rightarrow$ C14; Cg4: C8 $\rightarrow$ C9 $\rightarrow$ C10 $\rightarrow$ C11 $\rightarrow$ C13 $\rightarrow$ C14.



Fig. S5 Gradient isosurfaces (s = 0.5 a.u.) neighbouring units of Ca-ONDI (a) and Sr-ONDI (b). In order to clearly display the  $\pi$ - $\pi$  interactions between ligands, metal cations and water molecules were removed. The surfaces are colored on a blue-green-red (BGR) scale according to values of sign( $\lambda_2$ ) $\rho$ , ranging from -0.04 to 0.02 a.u. Blue indicates strong attractive interactions, green indicates moderate attractive interactions, and red indicates strong non-bonded overlap.

Reported CPs	Shortest π–π interaction distance (centroid–centroid) / Å
<b>PMC-1</b> <sup>14</sup>	3.402
<b>PMC-2</b> <sup>15</sup>	3.413
$[Zn(Gly-NDI)(DMF)_2]_n^{16}$	3.604
${[Sr(ntca)(H_2O)_2] \cdot H_2O]_n^{17}}$	3.754
$[Mn(\mu-pz)(\mu-Cl)_2]_n^{18}$	3.635
Sr-ONDI (this work)	3.437
Ca-ONDI(this work)	3.386

**Table S2** Comparison of the shortest  $\pi$ - $\pi$  interaction distance (centroid–centroid) among reported CPs with defined  $\pi$ - $\pi$  stacking structure.



Fig. S6 Hydrogen bonds and  $\pi-\pi$  interaction distances in H<sub>2</sub>ONDI·DMA and (Me<sub>2</sub>NH<sub>2</sub>)(HONDI).



Fig. S7 Band structure and DOS/PDOS of Sr-ONDI.



Fig. S8 Section of band structure near the Fermi level of Ca-ONDI (a) and Sr-ONDI (b)



Fig. S9 The *k* points paths in the Brillouin zone of the primitive cell of Ca-ONDI. (The Materials Studio software denotes the *k* point  $\Gamma$  as G.)



Fig. S10 Total and partial density of states of Ca-ONDI.



Fig. S11 Total and partial density of states of Sr-ONDI.



Fig. S12 The ligand arrangement type in Ca-ONDI (a) and in (Me<sub>2</sub>NH<sub>2</sub>)(HONDI) (b).

Item	$C=O_{\beta}$ (coordinated) / Å	C=O <sub>γ</sub> (free) / Å
Ca-ONDI	1.2271(23) 1.228(3)	1.2208(32) 1.2167(23)
Sr-ODNI	1.2229(128) 1.2233(159)	1.2366(164) 1.2271(128)

Fig. S13 Information on bond lengths of carbonyl groups in Ca-ONDI and Sr-ONDI.



**Fig. S14** Solid-state EPR spectra of **Ca-ONDI** and **Sr-ONDI**. Their very weak radical signals at the position of g=2.003 can be attributed to minor  $[M(ONDI)]^{\bullet-}$  impurities caused by the dimethylamine-rich mother liquor.[19]



**Fig. S15** PXRD pattern of (Me<sub>2</sub>NH<sub>2</sub>)(HONDI) (red) and the corresponding simulated diffraction pattern based on single crystal data (black).



**Fig. S16** Asymmetric unit of  $(Me_2NH_2)(HONDI)$ . The asymmetric unit consists of two  $Me_2NH_2^+$  cations and two halves of crystallographically independent anions. A hydrogen atom could be localized near O5, refinement results in the bond length O5–H5 1.03(6) Å. The distance O5…O2 2.591(4) Å is in agreement with an O5–H5…O2 hydrogen bond. Further hydrogen bonds are depicted in **Fig. S14**. Because it is unlikely that doubly deprotonated ONDI<sup>2–</sup> dianions are close to neutral H<sub>2</sub>ONDI molecules, the formula is given as (Me<sub>2</sub>NH<sub>2</sub>)(HONDI).



**Fig. S17** The I-V curves of H<sub>2</sub>ONDI·DMA (a) and (Me<sub>2</sub>NH<sub>2</sub>)(HONDI) (b) measured as pressed pellets. Compared to **Ca-ONDI** and **Sr-ONDI**, the electrical conductivities are relatively low. For H<sub>2</sub>ONDI·DMA, the lack of a continued charge transport path may contribute to its poor electrical

conductivity. As for the mono-deprotonated species,  $(Me_2NH_2)(HONDI)$ , the small  $\pi$ -overlap extent between neighboring naphthalene moieties could possibly be one of the reasons for low conductivity compared to **Ca-ONDI** and **Sr-ONDI**.

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