Influence of cation on charge transport and Schottky properties in mesaconate-bridged isostructural 1D coordination polymers

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Supporting Information

Experimental section

Materials and general methods

All chemicals were used as received from commercial suppliers without any further purification. High-purity cadmium(II) nitrate tetrahydrate and zinc(II) nitrate hexahydrate were specifically used for the crystallization process. All other reagents and solvents were of analytical reagent (AR) grade. Elemental analyses for carbon, hydrogen, and nitrogen (C, H, N) were carried out using a Perkin-Elmer 240C elemental analyzer. Infrared (IR) spectra were recorded using a Perkin-Elmer RX1 spectrometer in the range of 4000–500 cm^{-1} with samples prepared as KBr pellets.

Synthesis of CP1

The 4-avp ligand was first synthesized following a previously reported method.[1] To prepare the coordination polymer, a solution of 4-avp (0.113 g, 0.4 mmol) in methanol (2 mL) was carefully layered over a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.059 g, 0.2 mmol) in water (2 mL), using a 1:1 (v/v) methanol–water solution (2 mL) as the intermediate layer. Subsequently, a solution of mesaconic acid (H_2mes) (0.023 g, 0.2 mmol), neutralized with triethylamine (Et_3N) (0.021 g, 0.2 mmol) in ethanol (2 mL), was layered on top. After a week, light yellow, block-shaped crystals of $[Cd(4\text{-}avp)_2(mca)(H_2O)] \cdot H_2O$ (CP**1**) were obtained in 45% yield (0.077 g).Elemental analysis (%) calcd for $C_{47}H_{36}CdN_2O_6$: C, 67.43; H, 4.33; N, 3.35; found: C, 67.23; H, 4.23; N, 3.45. IR (KBr pellet, cm^{-1}): 1565 ν_{as} (COO^-), 1361 ν_{sys} (COO^-), 3069 ν(OH) and fingerprint region (<1500 cm-1).

Synthesis of CP2

CP**2** was synthesized using a similar procedure to that of CP**1**, with the key modifications being the use of $Zn(NO_3)_2 \cdot 6H_2O$ (0.062 g, 0.2 mmol) in place of $Cd(NO_3)_2 \cdot 4H_2O$ and substituting a 2 mL solution of DMF for the methanol–water mixture. After several days, light yellow, block-shaped crystals of and $[Zn(4\text{-}avp)_2(mca)(H_2O)] \cdot H_2O$ (CP**2**) were obtained in 60% yield (0.094 g). Elemental analysis (%) calcd for $C_{47}H_{38}N_2O_6Zn$: C, 71.26; H, 4.83; N, 3.54; found: C, 71.06; H, 4.73; N, 3.64. IR (KBr pellet, cm^{-1}): 1583 ν_{as} (COO^-), 1358 ν_{sys} (COO^-), 3046 ν(OH) and fingerprint region (<1500 cm^{-1}).

Table S1. Selected bond lengths (Å) in CP**1** and CP **2**

CP**1**	(Å)	CP**2**	(Å)
Cd(1)-O(1)	2.575(2)	Zn(1)-O(1)	2.036(5)
Cd(1)-O(2)	2.299(2)	Zn(1)-O(5)	2.091(3)
Cd(1)-O(5)	2.2753(18)	Zn(1)-N(1)	2.170(3)
Cd(1)-N(1)	2.3308(19)	Zn(1)-N(2)	2.162(3)
Cd(1)-N(2)	2.339(2)	$Zn(1)-O(3)_b$	2.334(5)
$Cd(1)-O(3)_a$	2.458(2)	$Zn(1)-O(4)_b$	2.181(5)
$Cd(1)-O(4)_a$	2.3591(18)		

Symmetry transformations used to generate equivalent atoms:
a = 1-x, -1/2+y, 3/2-z; b = 1-x, -1/2+y, 3/2-z.

Table S2. Selected bond angles (°) in CP**1**

O(1)-Cd(1)-O(2)	53.44(7)	O(5)-Cd(1)-N(1)	90.37(7)
O(1)-Cd(1)-O(5)	78.75(7)	O(5)-Cd(1)-N(2)	95.97(7)
O(1)-Cd(1)-N(1)	91.12(7)	$O(3)_a$-Cd(1)-O(5)	142.70(7)
O(1)-Cd(1)-N(2)	92.23(7)	$O(4)_a$-Cd(1)-O(5)	88.51(7)
$O(1)-Cd(1)-O(3)_a$	138.47(7)	N(1)-Cd(1)-N(2)	173.30(7)
$O(1)-Cd(1)-O(4)_a$	167.14(7)	$O(3)_a$-Cd(1)-N(1)	87.10(7)
O(2)-Cd(1)-O(5)	132.17(7)	$O(4)_a$-Cd(1)-N(1)	90.70(7)
O(2)-Cd(1)-N(1)	89.39(7)	$O(3)_a$-Cd(1)-N(2)	86.55(7)
O(2)-Cd(1)-N(2)	87.95(7)	$O(4)_a$-Cd(1)-N(2)	87.33(7)
$O(2)-Cd(1)-O(3)_a$	85.04(7)	$O(3)_a$-Cd(1)-$O(4)_a$	54.35(7)
$O(2)-Cd(1)-O(4)_a$	139.32(7)		

Symmetry transformations used to generate equivalent atoms: a = 1-x, -1/2+y, 3/2-z

Table S3. Selected bond angles (°) in CP**2**

O(1)-Zn(1)-O(5)	118.04(15)	$O(4)_b$-Zn(1)-O(5)	147.50(15)
O(1)-Zn(1)-N(1)	90.04(16)	N(1)-Zn(1)-N(2)	174.16(17)
O(1)-Zn(1)-N(2)	89.85(16)	$O(3)_b$-Zn(1)-N(1)	90.10(15)
O(1)-Zn(1)-$O(3)_b$	152.19(15)	$O(4)_b$-Zn(1)-N(1)	86.31(15)
O(1)-Zn(1)-$O(4)_b$	94.40(18)	$O(3)_b$-Zn(1)-N(2)	87.28(15)
O(5)-Zn(1)-N(1)	91.48(15)	$O(4)_b$-Zn(1)-N(2)	87.87(15)
O(5)-Zn(1)-N(2)	93.73(15)	$O(3)_b$-Zn(1)-$O(4)_b$	57.86(14)
$O(3)_b$-Zn(1)-O(5)	89.86(12)		

Symmetry transformations used to generate equivalent atoms: b = 1-x, -1/2+y, 3/2-z

Table S4. Hydrogen bonding in CP**1**

D—H···A	Distance (Å) D—H	Distance (Å) H···A	Distance (Å) D··A	Angle (°) ∠D—H···A
O(5)-H(5)A···O(6)	0.8700	1.8600	2.710 (3)	162.00
O(5)-H(5)B···O(4)	0.8700	1.8500	2.683(3)	158.00

Table S5. Hydrogen bonding in CP**2**

D—H···A	Distance (Å) D—H	Distance (Å) H···A	Distance (Å) D··A	Angle (°) ∠D—H···A
O(5)- H(5)A···O(2)	0.8800	2.5700	3.062(6)	117.00
O(5)- H(5)A···O(6)	0.8800	2.0900	2.859(6)	146.00
O(5)- H(5)B···O(3)	0.8800	1.9300	2.739(5)	152.00
O(6)- H(6)A···O(5)	0.8700	2.0700	2.859(6)	150.00
O(6)- H(6)B…..O(2)	0.8700	2.1400	2.845(7)	138.00

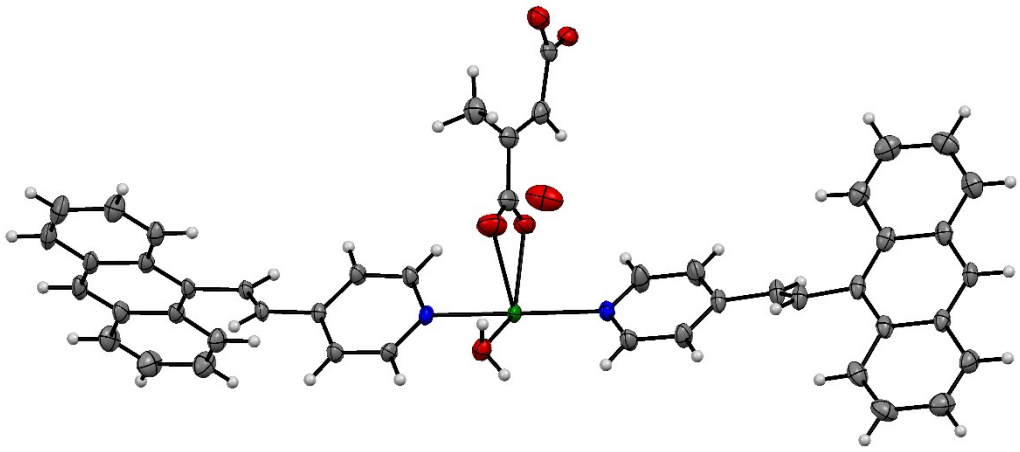

Fig. S1. Asymmetric unit of CP**1** with 50% ellipsoid probability. Color scheme: carbon (gray), oxygen (red), nitrogen (blue), and cadmium (deep green).

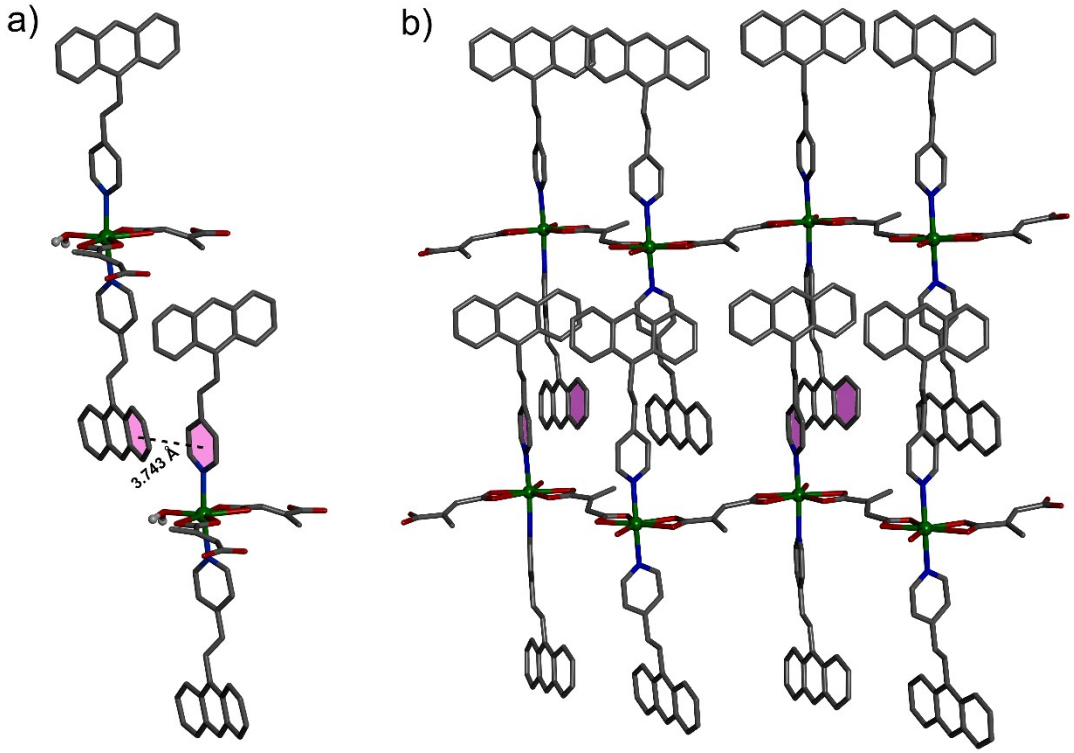

Fig. S2. a) Supramolecular synthon and b) 2D network formed by intermolecular π···π interactions in CP**1**. Only selected atoms are shown for the clarity.

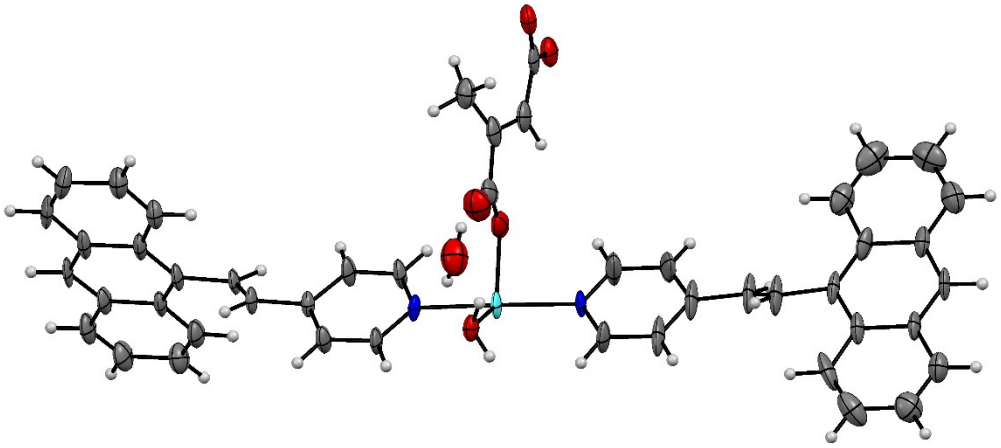

Fig. S3. Asymmetric unit of CP**2** with 50% ellipsoid probability. Color scheme: carbon (gray), oxygen (red), nitrogen (blue), and zinc (cyan green).

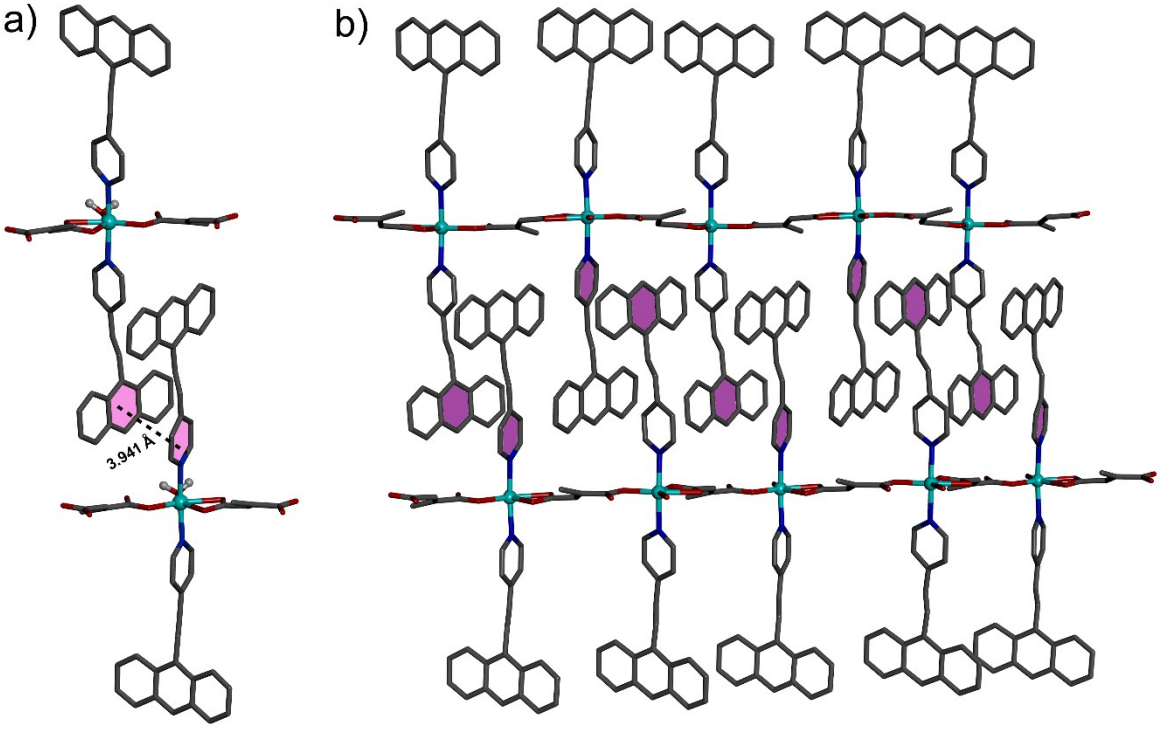

Fig. S4. a) Supramolecular synthon and b) 2D network formed by intermolecular π···π interactions in CP**2**. Only selected atoms are shown for the clarity.

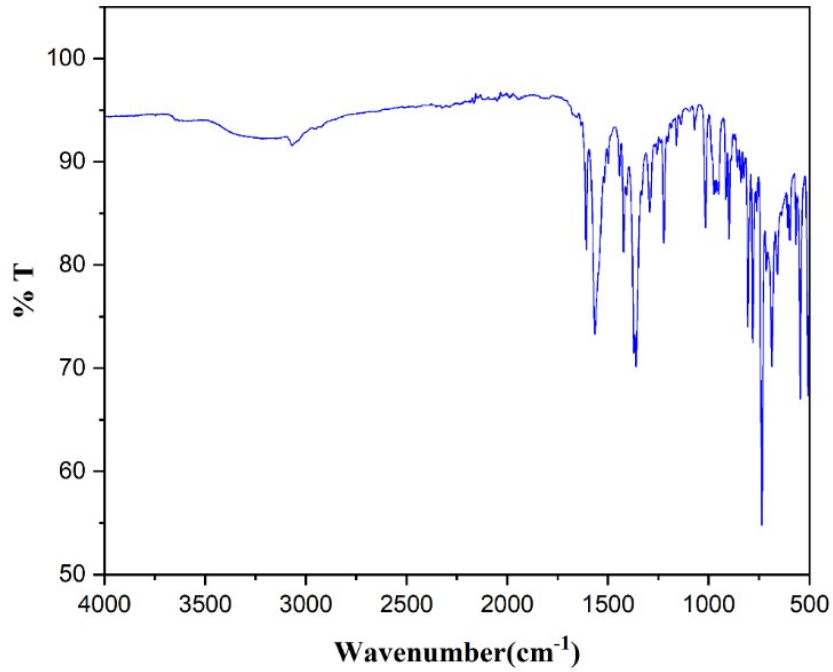

Fig. S5. IR spectrum of CP**1**.

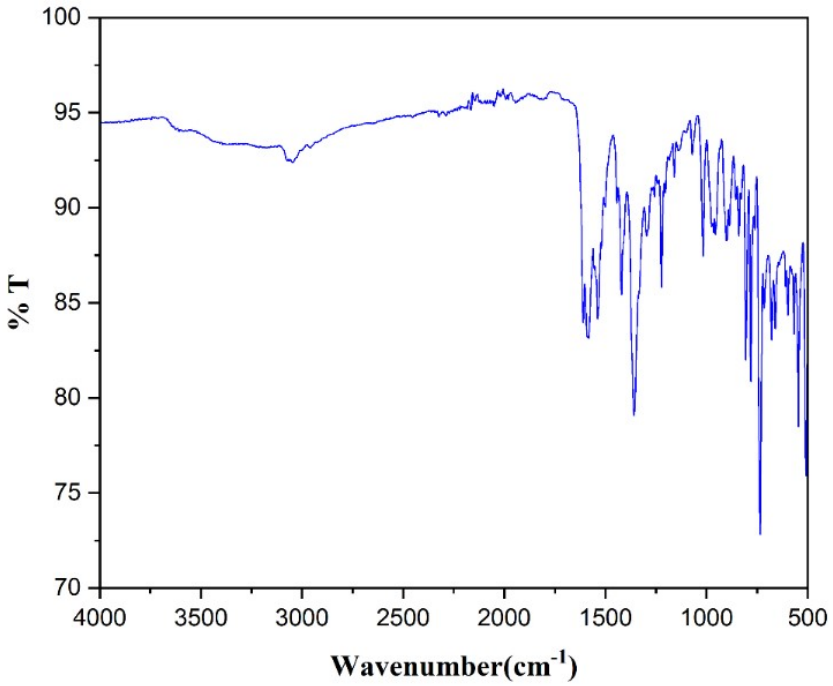

Fig. S6. IR spectrum of CP**2**.

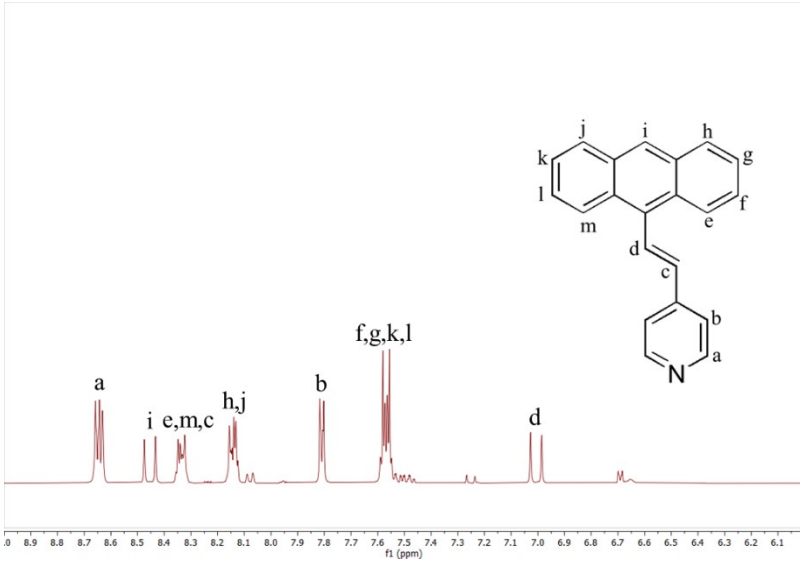

Fig. S7. [1]HNMR spectrum of CP**1**.

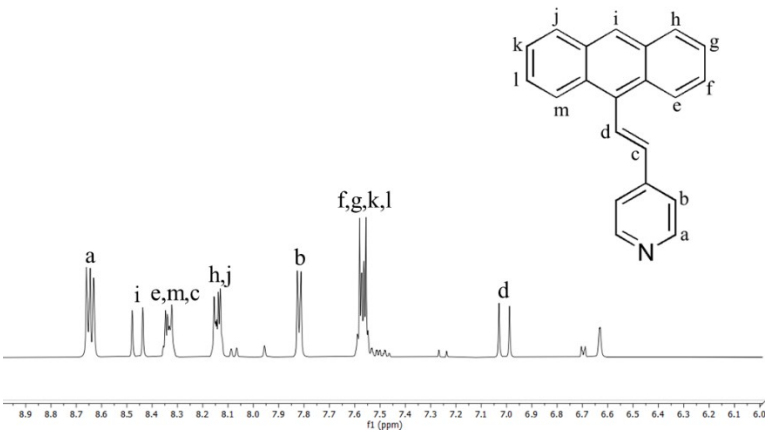

Fig. S8. [1]HNMR spectrum of CP**2**.

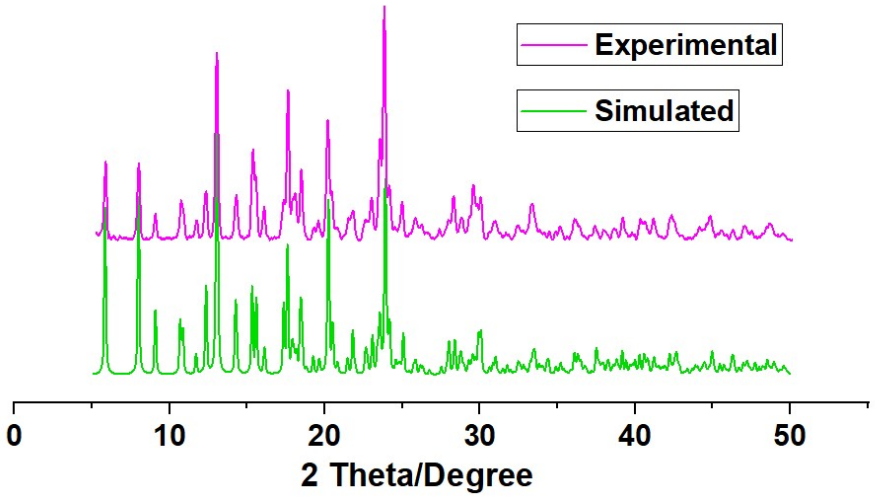

Fig. S9. PXRD of CP**1** simulated (green) and experimental (pink).

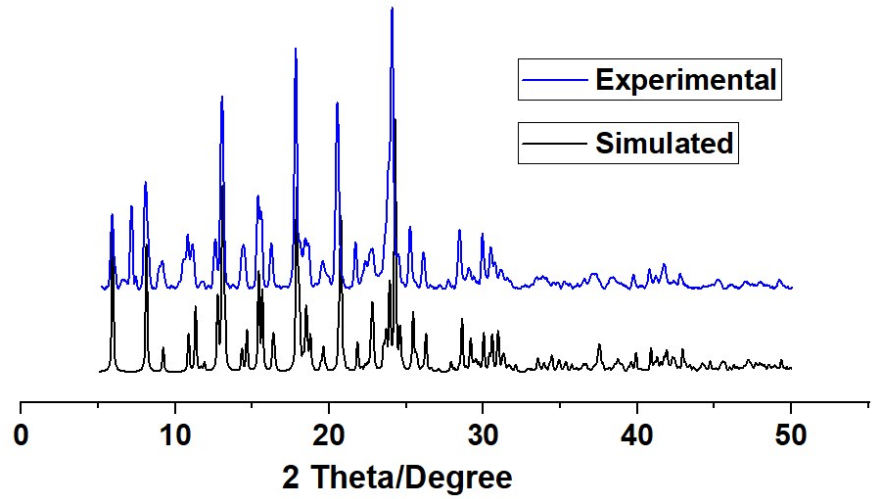

Fig. S10. PXRD of CP**2** simulated (black) and experimental (blue).

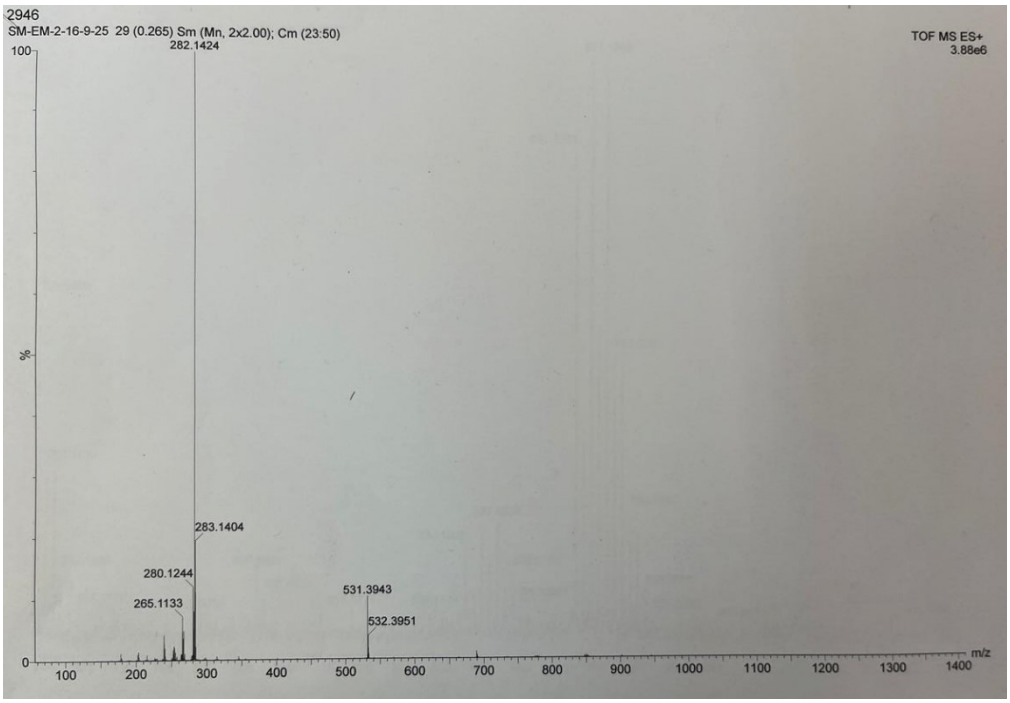

Fig. S11. Mass spectrum of CP**1**.

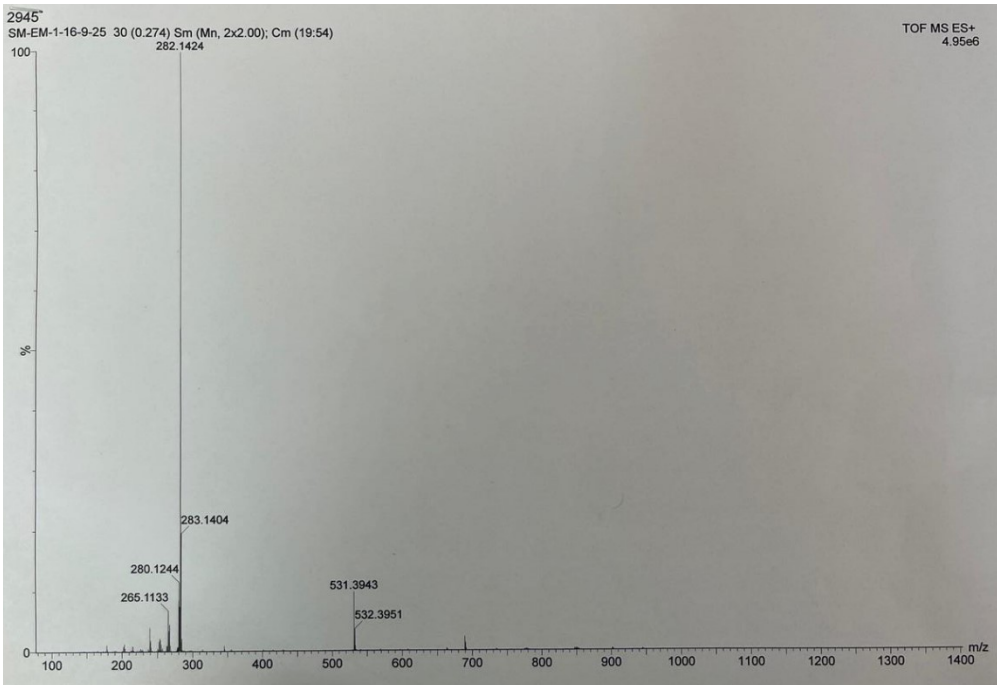

Fig. S12. Mass spectrum of CP**2**.

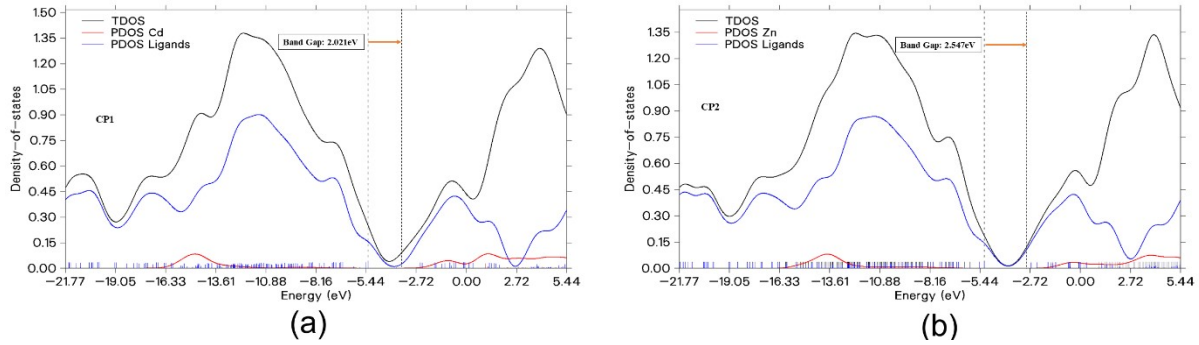

Fig. S13. TDOS and PDOS plots of (a) CP**1** and (b) CP**2**.

Table S6. Previously reported conductance properties of conductive CPs

Sl. No.	Compounds	Conductivity (S m^{-1})	Ref
1.	$\{[Cd_2(tppz)(2\text{-}ATPA)_2(H_2O)_2]\cdot(MeOH)_2\}_n$ (CP**1**), [tppz = 2,3,5,6-tetrakis(2-pyridyl)-pyrazine and H_2ATPA = 2-amino terephthalic acid]	3.76×10^{-6}	2
2.	[Cd(tppz)(adc)(MeOH)] (**1**) [Cd(tppz)(trep)] (**2**) [Cd(tppz)(2,6-ndc)] (**3**) [H_2adc = acetylenedicarboxylic acid, H_2trep = terephthalic acid and H_2ndc = 2,6-naphthalene dicarboxylic acid]	4.72×10^{-5} 1.10×10^{-4} 1.12×10^{-4}	3
4.	$[Zn(mes)(pcih)(H_2O)_2]_n$ (**1**) [H_2mes = mesaconic acid and pcih = pyridine-4-carboxaldehydeiso-nicotinoyl hydrazine]	2.98×10^{-4}	4
5.	$[Zn(cis\text{-}1,4\text{-}chdc)(4\text{-}phpy)]_n$ (**1**) $[Zn(cis\text{-}1,4\text{-}chdc)(py)]_n$ (**2**) [1,4-H_2chdc = 1,4-cyclohexane dicarboxylic acid, 4-phpy = 4-phenylpyridine and py = pyridine]	1.09×10^{-3} 6.01×10^{-5}	5
6.	$[\{Cd_2(cis\text{-}1,4\text{-}chdc)_2(1,10\text{-}phen)_2\}\cdot 5H_2O]_n$ (**1**) $\{Zn(cis\text{-}1,4\text{-}chdc)(1,10\text{-}phen)(H_2O)\}_n$ (**2**) [1,10-phen = 1,10-phenanthroline]	7.51×10^{-4} 2.52×10^{-4}	6
7.	$[Zn(4\text{-}avp)_2(5\text{-}nip)]\cdot(solvent)_x$ (**1**)	1.46×10^{-4}	7

	and [Cd(4-avp)(5-nip).CH_3OH] (**2**) 4-avp = (4-[2-(9-anthryl)vinyl]pyridine and $H_2$5-nip = bidentate linker 5-nitroisophthalic acid	6.33×10^{-4}	
9.	[Cd(4-avp)$_2$(mes)(H_2O)]·H_2O (**1**) and [Zn(4-avp)$_2$(mes)(H_2O)]·H_2O (**2**)	1.39×10^{-3} 3.71×10^{-4}	**This work**

References

1. C. W. Chan, T. F. Lai, C.M. Che, and S. M. Peng, *J. Am. Chem. Soc.,* 1993, **115**, 11245-11253.
2. A. Patra, S. Bhunia, P. Das, G. Bairy, P. P. Ray and C. Sinha, *Cryst. Growth Des.,* 2024, **24**, 10171-10181.
3. S. Bhunia, D. Sahoo, B. Dutta, S. Maity, N. B. Manik and C. Sinha, *Inorg. Chem.,* 2023, **62**, 20948-20960.
4. M. Shit, A. K. Karan, D. Sahoo, N. B. Manik, B. Dutta, and C. Sinha, *New J Chem*., 2023, **47**, 5922-5929.
5. P. Das, S. Khan, S. Maity, S. Naaz, S. Islam, P. Ghosh and M. H. Mir, *New J Chem*., 2019, **43**, 16071-16077.
6. B. Pal, S. Khan, B. Dutta, S. Naaz, S. Maity, P. Ghosh, and M. H. Mir, *CrystEngComm.*, 2021, **23**, 7525-7533.
7. E. Hossain, R. Sk, M. Das, J. Goura, S. Roy, P. P. Ray, M. H. Mir and S. Mukhopadhyay, *Eur. J. Inorg. Chem.,* 2024, **27**, e202300736.