Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Effect on Schottky behavior of 1D coordination polymers by altering para-substituent on the benzoate ligands

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Supporting Information

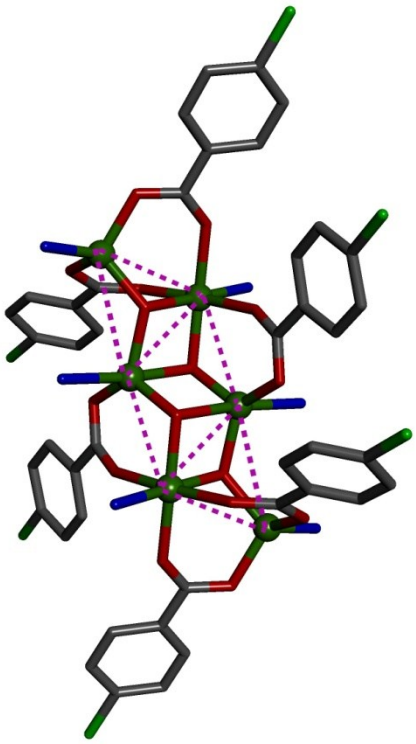


Fig. S1 A view of chair-like hexagonal {Zn6} unit in compound **1**.

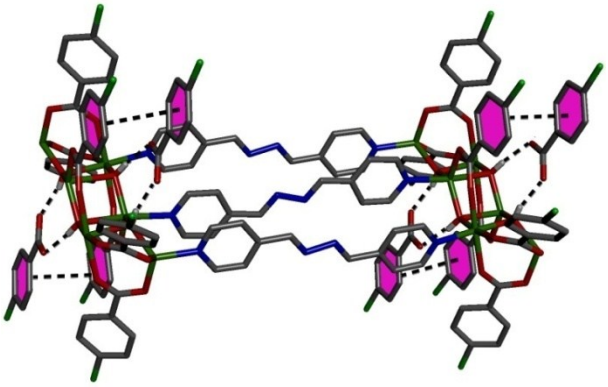
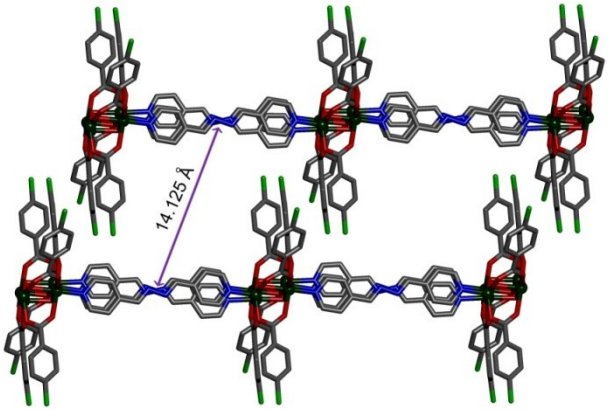
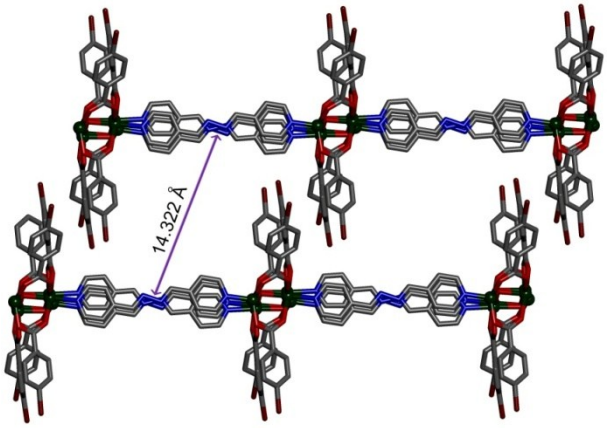


Fig. S2 Hydrogen bonding and π···π interactions between lattice 4-clba and {Zn6} unit in compound **1**.



(a)



(b)

Fig. S3 The perspective view of compound (a) **1** and (b) **2** showing the distance between the adjacent 1D chains.

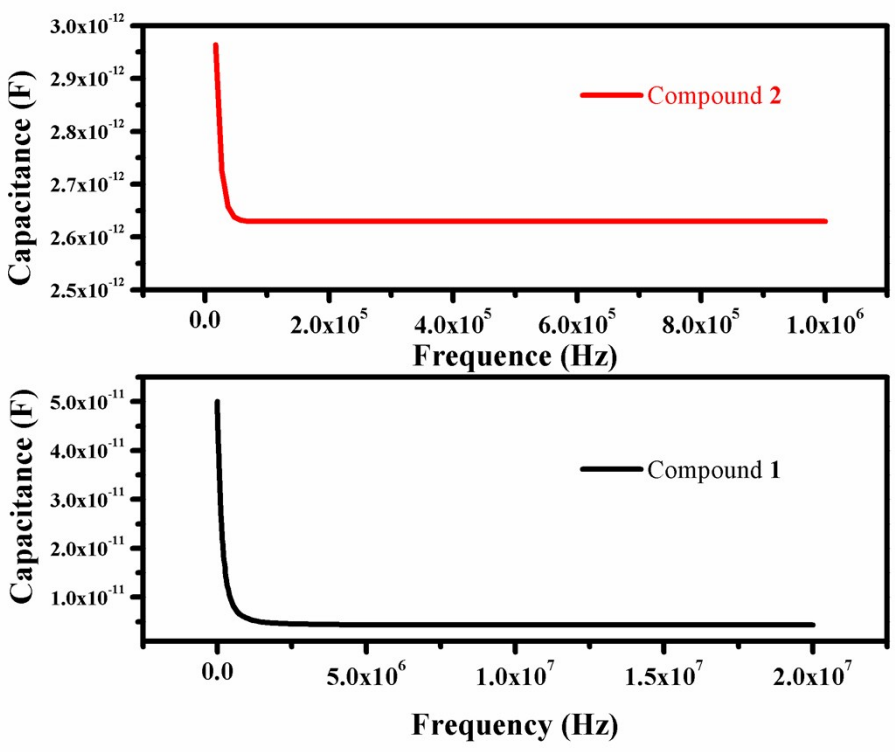


Fig. S4 Capacitance–frequency plot for the determination of dielectric constant.

Here, Fig. S4 illustrates that the capacitance is saturated at high frequency. Using this saturated capacitance, we have calculated the relative permittivity with the help of the following relation:

$$\varepsilon_r = C_{sat} L / \varepsilon_0 A \qquad (1)$$

where C_{sat} is the saturated capacitance at high frequency, L is the length, ε_0 is the permittivity at free space and A is the effective area of the film of the compounds.

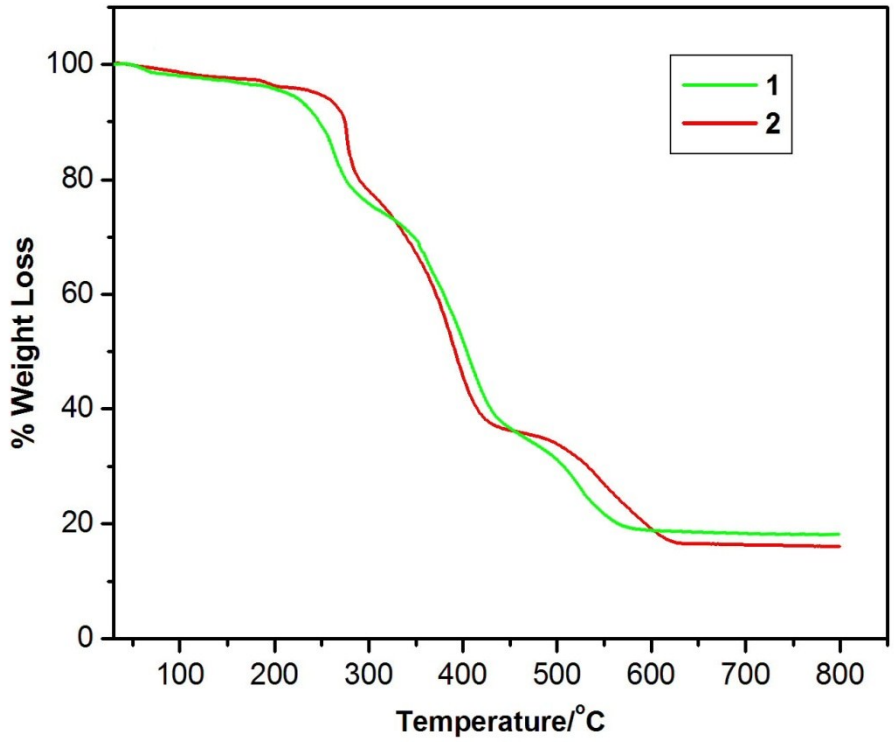


Fig. S5 TGA plot of compound **1** (green) and **2** (red) measured under N_2 atmosphere.

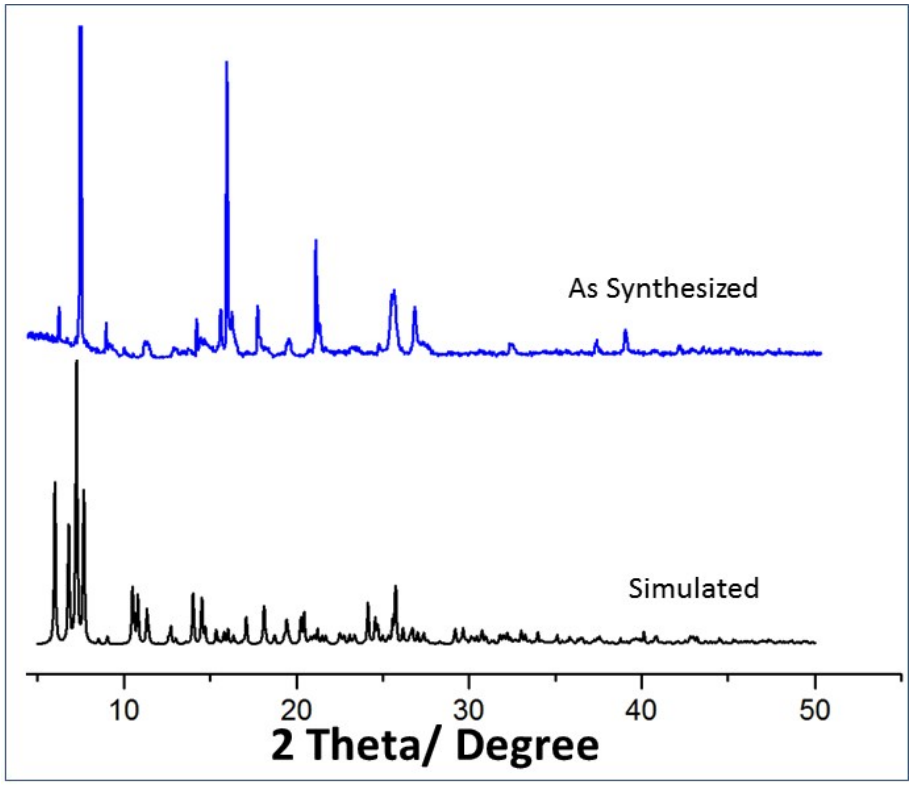


Fig. S6 PXRD patterns of simulated **1** (black) and as-synthesized **1** (blue).

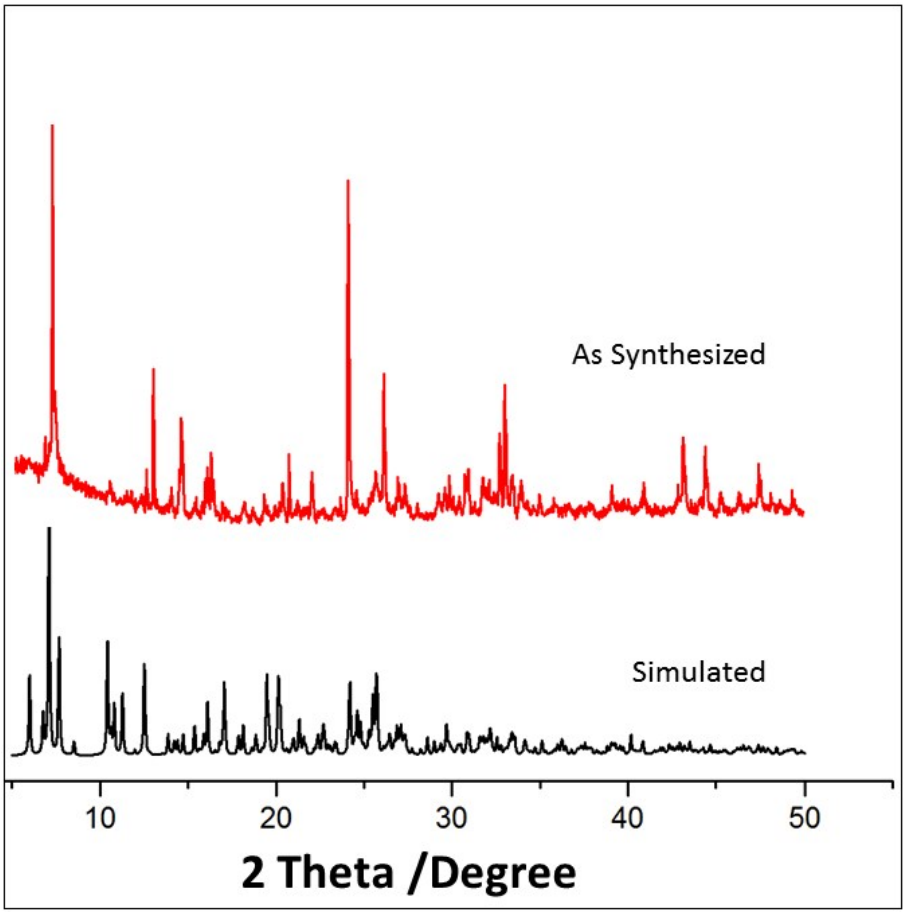


Fig. S7 PXRD patterns of simulated **2** (black) and as-synthesized **2** (red).

Table S1 Crystal data and refinement parameters for compound **1** and **2**

Formula	$C_{93}H_{69}Cl_8N_{12}O_{21}Zn_6$ (**1**)	$C_{93}H_{66}Br_8N_{12}O_{21}Zn_6$ (**2**)
Fw	2366.54	2719.12
cryst syst	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.0190(3)	12.0085(7)
b (Å)	14.1254(2)	14.3222(8)
c (Å)	16.0929(4)	16.2643(9)
α(deg)	109.0940(17)	110.576(2)
β(deg)	100.0158(19)	100.003(2)
γ (deg)	98.6977(16)	98.071(2)
V (Å^3)	2478.07(9)	2516.7(2)
Z	1	1
D_{calcd}(g/cm^3)	1.586	1.794
μ(mm^{-1})	4.218	4.656
λ(Å)	1.54184	0.71073
data[$I > 2\sigma(I)$]/params	8846/741	8340/643
GOF on F^2	1.025	1.090
final R indices[$I > 2\sigma(I)$][a,b]	$R1$ = 0.0436	$R1$ = 0.0704
	$wR2$ = 0.1230	$wR2$ = 0.1564

[a] $R1 = \Sigma||F_o| \quad |F_c||/ \Sigma|F_o|$, [b] $wR2 = [\Sigma w(F_o^2 \quad F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths and bond angles in **1**

Zn(1)-O(22)	1.997(2)	Zn(1)-O(45)b	2.2091(19)
Zn(2)-O(31)b	2.122(2)	Zn(3)-O(41)	1.942(2)
Zn(1)-O(44)	2.000(2)	Zn(2)-O(21)	2.151(2)
Zn(2)-(42)b	2.201(2)	Zn(3)-O(44)	1.9301(19)
Zn(1)-O(45)	1.968(2)	Zn(2)-O(45)	2.0318(19)
Zn(2)-O(44)b	2.0940(19)	Zn(3)-N(46)	2.031(2)
Zn(1)-N(62)	2.197(2)	Zn(2)-N(56)a	2.101(2)
Zn(3)-O(32)	1.942(2)	O(22)-Zn(1)-O(44)	125.92(9)
O(22)-Zn(1)-O(45)b	88.39(8)	O(44)-Zn(1)-O(45)b	81.53(7)
O(22)-Zn(1)-O(45)	126.51(9)	O(44 -Zn(1)-O(45)	105.19(8)
O(45)-Zn(1)-N(62)	101.99(9)	O(22)-Zn(1)-N(62)	89.52(9)
O(44)-Zn(1)-N(62)	94.80(8)	O(45)-Zn(1)-O(45)b	84.13(8)
N(62)-Zn(1)-O(45)b	173.56(8)	O(21)-Zn(2)-O(31)b	84.98(9)
O(45)-Zn(2)-N(56)a	96.58(9)	O(45)-Zn(2)-O(44)b	83.69(7)
N(56)a-Zn(2)-O(44)b	177.99(9)	O(42)b-Zn(2)-O(44)b	86.39(8)
O(32)-Zn(3)-N(46)	101.99(10)	O(44)-Zn(3)-N(46)	112.93(9)
O(21)-Zn(2)-O(45)	89.57(9)	O(21)-Zn(2)-O(42)b	176.09(9)
O(45)-Zn(2)-O(31)b	172.49(9)	N(56)a-Zn(2)-O(31)b	88.75(9)
O(31)b-Zn(2)-O(42)b	97.38(9)	O(32)-Zn(3)-O(41)	121.68(10)
O(41)-Zn(3)-O(44)	106.75(9)	O(21)-Zn(2)-N(56)a	91.56(10)
O(21)-Zn(2)-O(44)b	90.44(9)	O(45)-Zn(2)-O(42)b	87.80(8)
N(56)a-Zn(2)-O(42)b	91.62(9)	O(31)b-Zn(2)-O(44)b	91.18(8)
O(32)-Zn(3)-O(44)	107.69(9)	O(41)-Zn(3)-N(46)	105.90(9)

Symmetry Code: a = -x, 1-y, 1-z; 1-x, 2-y, 2-z

Table S3 Selected bond lengths and bond angles in **2**

Zn(2)-O00D	1.991(6)	Zn(2)-O7	2.000(5)
Zn(3)-O009	2.038(5)	Zn(3)-O00F	2.154(6)
Zn(3)-O7a	2.098(5)	Zn(3)-N00Jb	2.110(7)
Zn(5)-O7	1.925(5)	Zn(5)-N1	2.031(6)
Zn(2)-N2	2.192(7)	Zn(3)-O00Ca	2.196(6)
Zn(5)-O00A	1.942(6)	Zn(2)-O009	1.969(5)
Zn(2)-O009a	2.210(5)	Zn(3)-O00Ea	2.133(6)
Zn(5)-O00B	1.939(6)	O009-Zn(2)-O00D	126.5(2)
O009-Zn(2)-O009a	84.6(2)	O00D-Zn(2)-O009a	87.7(2)
N2-Zn(2)-O009a	173.8(2)	O009-Zn(2)-O7	105.2(2)
O00D-Zn(2)-O7	125.9(2)	O7-Zn(2)-N2	95.2(2)
O009-Zn(3)-O00F	89.4(2)	O009- Zn(2)-N2	101.5(2)
O00D-Zn(2)- N2	89.6(3)	O7- Zn(2)-O009a	81.98(19)
O009-Zn(3)-O00Ca	88.0(2)	O009-Zn(3)-O00Ea	172.6(2)
O00F-Zn(3)-O00Ca	176.5(2)	O00F-Zn(3)-N00Jb	91.4(3)
O00Ca-Zn(3)-N00Jb	91.2(3)	O7a-Zn(3)- N00Jb	178.1(3)
O00A-Zn(5)-N1	102.0(3)	O7-Zn(5)-N1	113.0(3)
O009-Zn(3)-O7a	83.94(19)	O00F-Zn(3)-O00Ea	85.3(3)
O00Ca-Zn(3)-O00Ea	97.1(3)	O00Ea-Zn(3)-O7a	91.0(2)
O00A-Zn(5)-O00B	122.0(3)	O00B-Zn(5)-O7	107.2(2)
O009-Zn(3)-N00Jb	96.6(2)	O00F -Zn(3)-O7a	90.5(2)
O00Ca-Zn(3)-O7a	86.9(2)	O00Ea-Zn(3)-N00Jb	88.7(2)
O00A-Zn(5)-O7	107.2(3)	O00B-Zn(5)-N1	105.5(3)

Symmetry Code: a = 1-x, -y, -z; b = 2-x, 1-y, 1-z

Table S4 Hydrogen bonding interactions of compound **1** and **2**.

Compound	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	<D-H···A (°)
1	O(44)-H(44)···O(12)	0.71(5)	1.93(5)	2.625(4)	166(5)
	O(45)-H(45)···O(11)	0.81(5)	2.11(5)	2.899(3)	163(5)
	C(5)-H(5)···O(1)	0.86(6)	2.55(6)	3.176(12)	131(5)
	C(5)-H(5)···O(11)	0.86(6)	2.47(6)	2.823(6)	105(5)
	C(15)-H(15)···O(21)	0.95(4)	2.39(4)	2.765(4)	103(3)
	C(19)-H(19)···O(22)	0.84(5)	2.49(5)	2.804(5)	104(4)
	C(25)-H(25)···O(32)	0.93	2.42	2.744(5)	100
	C(51)-H(51)···O(12)	0.87(5)	2.52(4)	3.231(4)	140(4)
	C(57)-H(57)···O(42)	0.93	2.50	3.110(4)	124
	C(58)-H(58)···O(1)	0.93	2.49	2.992(11)	114
	C(61)-H(61)···O(21)	0.93	2.52	3.056(4)	117
	C(63)-H(63)···O(11)	0.92(5)	2.47(5)	3.377(4)	171(3)
	C(67)-H(67)···O(22)	0.92(4)	2.40(4)	3.035(4)	126(4)
2	O(2)-H(2A)···O(00K)	0.82	1.94	2.71(3)	154
	C(00T)-H(00T)···O(00H)	0.93	2.51	3.247(11)	137
	C(00V)-H(00V)···O(00K)	0.93	2.45	3.371(13)	171
	C(00W)-H(00W)···O(00D)	0.93	2.45	3.021(11)	119
	C(017)-H(017)···O(00F)	0.93	2.51	3.055(10)	118
	C(01A)-H(01A)···O(00C)	0.93	2.49	3.089(11)	123
	C(01F)-H(01F)···O(2)	0.93	2.52	3.01(3)	113
	C(01T)-H(01T)···O(00A)	0.93	2.41	2.730(14)	100
	C(01W)-H(01W)···O(2)	0.93	2.46	3.12(3)	128

Table S5 Halogen bonding interactions of compounds **1** and **2**

Compound	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	<D-H···A (°)
1	C(47)-H(47)···Cl(23)	0.97(5)	2.79(5)	3.489(3)	130(4)
2	C(00X)-H(00X)···Br(2)	0.93	2.81	3.575(9)	141

Table S6 $\pi\cdots\pi$ interactions in **1** and **2**

Compound	Ring(i) → Ring(j)	Distance between the (i,j) ring centroids (Å) in the crystal
1	R(1)→R(2)	3.680
	R(2)→R(3)	3.900
2	R(4)→R(5)	3.686
	R(5)→R(6)	3.857

R(j) denotes the j-th ring: R(1) = N(46)/C(51)/C(50)/C(49)/C(48)/C(47);
R(2) = N(62)/C(63)/C(64)/C(65)/C(66)/C(67);
R(3) = N(56)/C(57)/C(58)/C(59)/C(60)/C(61);
R(4) = N(1)/C(00T)/C(013)/C(00P)/C(00Y)/C(00X);
R(5) = N(2)/C(00V)/C(01E)/C(010)/C(015)/C(00W)
R(6) = N(00J)/C(01A)/C(01F)/C(00U)/C(018)/C(017)

Table S7. Table for comparing conductivity data.

Sample Name	**Electrical conductivity**	**Reference**
$[Cd(4\text{-bpd})(SCN)_2]_n$	2.90×10^{-4} S m^{-1}	1
$Cd(adc)(4\text{-phpy})_2(H_2O)_2]_n$	1.53×10^{-7} S cm^{-1}	2
$Cd(adc)(4\text{-phpy})_2(H_2O)_2]_n$	5.90×10^{-8} S cm^{-1}	2
$[Cd(3\text{-bpd})(SCN)_2]_n$	4.53×10^{-7} S cm^{-1}	3
$[Zn_2(DPBEIH)(H_2O)_2]_n$	8.42×10^{-7} S m^{-1}	4
$[Cd_2(DPBEIH)(H_2O)_2]_n$	5.04×10^{-6} S m^{-1}	4
$[Zn_6(bpd)_3(p\text{-clba})_6(\mu_3\text{-OH})_4]\cdot(p\text{-clba})_2\cdot(CH_3OH)$	3.29×10^{-4} S m^{-1}	Compound **1**
$[Zn_6(bpd)_3(p\text{-brba})_6(\mu_3\text{-OH})_4]\cdot(p\text{-brba})_2\cdot(CH_3OH)$	2.22×10^{-4} S m^{-1}	Compound **2**

References

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4. J. T. Makode, A. R. Yaul, S. G. Bhadange and A. S. Aswar, *Russ. J. Inorg. Chem*. 2009, **54**, 1372–1377.