Electronic Supplementary Information

Site-selective homo- and hetero-metallic doping of a 1D Zn-based coordination polymer to enhance the dimensionality and photocurrent responses

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Table S1 Selected bond lengths (Å) and angles (°) for **2** and **2a**−**2c**.

Compound **2**			
Zn(1)-O(1)	1.9307(12)	Zn(1)-O(5A)	1.9264(13)
Zn(1)-O(7)	1.9875(14)	Zn(1)-N(1)	2.0112(15)
Zn(2)-O(3B)	2.0734(12)	Zn(2)-O(3)	2.0734(12)
Zn(2)-O(8)	2.1864(13)	Zn(2)-O(8B)	2.1864(13)
Zn(2)-O(9)	2.0514(14)	Zn(2)-O(9B)	2.0514(14)
O(1)-Zn(1)-O(7)	107.57(6)	O(1)-Zn(1)-N(1)	116.66(6)
O(5A)-Zn(1)-O(1)	111.50(6)	O(5A)-Zn(1)-O(7)	115.30(6)
O(5A)-Zn(1)-N(1)	105.51(6)	O(7)-Zn(1)-N(1)	100.08(6)
O(3)-Zn(2)-O(3B)	180.000(1)	O(3)-Zn(2)-O(8)	89.04(5)
O(3B)-Zn(2)-O(8B)	89.04(5)	O(3)-Zn(2)-O(8B)	90.96(5)
O(3B)-Zn(2)-O(8)	90.96(5)	O(8)-Zn(2)-O(8B)	180.000(1)
O(9)-Zn(2)-O(3)	89.22(6)	O(9B)-Zn(2)-O(3)	90.78(6)
O(9B)-Zn(2)-O(3B)	89.22(6)	O(9)-Zn(2)-O(3B)	90.78(6)
O(9)-Zn(2)-O(8B)	88.03(5)	O(9B)-Zn(2)-O(8B)	91.97(5)
O(9)-Zn(2)-O(8)	91.97(5)	O(9B)-Zn(2)-O(8)	88.03(5)
O(9B)-Zn(2)-O(9)	180.000(1)		
Compound **2a**			
Zn(1)-O(1)	1.9298(17)	Zn(1)-O(5A)	1.9268(17)
Zn(1)-O(7)	1.9874(19)	Zn(1)-N(1)	2.012(2)
Zn(2)-O(3B)	2.0719(17)	Zn(2)-O(3)	2.0734(12)
Zn(2)-O(8)	2.1819(13)	Zn(2)-O(8B)	2.1819(13)
Zn(2)-O(9)	2.0515(18)	Zn(2)-O(9B)	2.0515(18)
O(1)-Zn(1)-O(7)	107.42(8)	O(1)-Zn(1)-N(1)	116.72(8)
O(5A)-Zn(1)-O(1)	111.56(7)	O(5A)-Zn(1)-O(7)	115.53(8)
O(5A)-Zn(1)-N(1)	105.36(8)	O(7)-Zn(1)-N(1)	100.02(8)
O(3)-Zn(2)-O(3B)	180.000(1)	O(3)-Zn(2)-O(8)	89.02(7)
O(3B)-Zn(2)-O(8B)	90.98(7)	O(3)-Zn(2)-O(8B)	90.98(7)
O(3B)-Zn(2)-O(8)	90.98(7)	O(8)-Zn(2)-O(8B)	180.000(1)
O(9)-Zn(2)-O(3)	90.86(7)	O(9B)-Zn(2)-O(3)	90.86(7)
O(9B)-Zn(2)-O(3B)	89.14(7)	O(9)-Zn(2)-O(3B)	90.86(7)
O(9)-Zn(2)-O(8B)	88.14(7)	O(9B)-Zn(2)-O(8B)	91.86(7)
O(9)-Zn(2)-O(8)	91.86(7)	O(9B)-Zn(2)-O(8)	88.14(7)
O(9B)-Zn(2)-O(9)	180.000(1)		
Compound **2b**			
Zn(1)-O(1)	1.9234(17)	Zn(1)-O(5A)	1.9212(17)
Zn(1)-O(7)	1.991(2)	Zn(1)-N(1)	2.006(2)
Zn(2)-O(3B)	2.0748(16)	Zn(2)-O(3)	2.0748(16)
Zn(2)-O(8)	2.1746(19)	Zn(2)-O(8B)	2.1746(19)
Zn(2)-O(9)	2.0595(19)	Zn(2)-O(9B)	2.0595(19)
O(1)-Zn(1)-O(7)	106.94(8)	O(1)-Zn(1)-N(1)	117.01(8)

O(5A)-Zn(1)-O(1)	112.10(8)	O(5A)-Zn(1)-O(7)	115.48(9)
O(5A)-Zn(1)-N(1)	105.26(8)	O(7)-Zn(1)-N(1)	99.77(8)
O(3)-Zn(2)-O(3B)	180.000(1)	O(3)-Zn(2)-O(8)	89.21(7)
O(3B)-Zn(2)-O(8B)	89.21(7)	O(3)-Zn(2)-O(8B)	90.79(7)
O(3B)-Zn(2)-O(8)	90.79(7)	O(8)-Zn(2)-O(8B)	180.000(1)
O(9)-Zn(2)-O(3)	89.04(8)	O(9B)-Zn(2)-O(3)	90.96(8)
O(9B)-Zn(2)-O(3B)	89.04(8)	O(9)-Zn(2)-O(3B)	89.04(8)
O(9)-Zn(2)-O(8B)	87.86(8)	O(9B)-Zn(2)-O(8B)	92.14(8)
O(9)-Zn(2)-O(8)	92.14(8)	O(9B)-Zn(2)-O(8)	87.86(8)
O(9B)-Zn(2)-O(9)	180.000(1)		
Compound **2c**			
Zn(1)-O(1)	1.9279(13)	Zn(1)-O(5A)	1.9282(13)
Zn(1)-O(7)	1.9881(14)	Zn(1)-N(1)	2.0121(16)
Co(1)-O(3B)	2.0820(13)	Co(1)-O(3)	2.0820(13)
Co(1)-O(8)	2.1619(14)	Co(1)-O(8B)	2.1619(14)
Co(1)-O(9)	2.0541(14)	Co(1)-O(9B)	2.0541(14)
O(1)-Zn(1)-O(7)	107.63(6)	O(1)-Zn(1)-N(1)	116.53(6)
O(5A)-Zn(1)-O(1)	111.57(6)	O(5A)-Zn(1)-O(7)	115.67(6)
O(5A)-Zn(1)-N(1)	105.23(6)	O(7)-Zn(1)-N(1)	99.98(6)
O(3)- Co(1)-O(3B)	180.0	O(3)- Co(1)-O(8)	89.15(5)
O(3B)- Co(1)-O(8B)	89.15(5)	O(3)- Co(1)-O(8B)	90.85(5)
O(3B)- Co(1)-O(8)	90.85(5)	O(8)- Co(1)-O(8B)	180.000(1)
O(9)-Co(1)-O(3)	88.72(6)	O(9B)-Co(1)-O(3)	91.28(6)
O(9B)-Co(1)-O(3B)	88.72(6)	O(9)-Co(1)-O(3B)	91.28(6)
O(9)-Co(1)-O(8B)	88.40(6)	O(9B)-Co(1)-O(8B)	91.60(6)
O(9)-Co(1)-O(8)	91.60(6)	O(9B)-Co(1)-O(8)	88.40(6)
O(9B)-Co(1)-O(9)	180.000(1)		

Symmetry codes for A : $1 - x$, $1 - y$, $1 - z$; B: $1 - x$, $1 - y$, $2 - z$.

Table S2 Hydrogen bond lengths (Å) and angles (°) for **2** and **2a−2c**.

D-H···A	D-H	H···A	D···A	D-H···A	Symmetrical codes
2					
O(7)-H(7A)···O(2)	0.81(3)	1.88(3)	2.690(2)	174(2)	$1 + x, y, z$
O(7)-H(7B)···O(8)	0.75(3)	1.93(3)	2.680(2)	178(3)	
O(8)-H(8A)···O(4)	0.82(2)	1.81(3)	2.610(2)	164(2)	$1 - x, 1 - y, 2 - z$
O(8)-H(8B)···O(12)	0.82(2)	1.96(3)	2.766(2)	168(2)	$1 - x, 1 - y, 1 - z$
O(9)-H(9A)···O(10)	0.80(3)	1.92(3)	2.709(2)	167(2)	$1 - x, 1 - y, 2 - z$
O(9)-H(9B)···O(11)	0.80(3)	1.93(3)	2.732(2)	174(3)	$-1 + x, y, z$
O(11)-H(11A)···O(2)	0.79(3)	2.09(3)	2.821(2)	154(3)	$1 + x, y, z$
O(11)-H(11B)···O(4)	0.77(3)	2.10(3)	2.865(2)	168(3)	$1 - x, 1 - y, 2 - y$
O(12)-H(12A)···O(6)	0.81(3)	1.97(3)	2.765(2)	165(2)	
O(12)-H(12B)···O(11)	0.79(3)	2.01(3)	2.748(2)	156(2)	$2 - x, 1 - y, 1 - z$
N(2)-H(2)···O(12)	0.86	2.02	2.872(2)	171	$2 - x, - y, 1 - x$
2a					
O(7)-H(7A)···O(2)	0.79(3)	1.90(3)	2.688(3)	170(3)	$1 + x, y, z$
O(7)-H(7B)···O(8)	0.81(3)	1.88(3)	2.679(3)	172(3)	
O(8)-H(8A)···O(4)	0.85(3)	1.78(3)	2.609(3)	162(3)	$1 - x, 1 - y, 2 - z$
O(8)-H(8B)···O(12)	0.82(3)	1.96(3)	2.768(3)	167(3)	$1 - x, 1 - y, 1 - z$
O(9)-H(9A)···O(10)	0.80(3)	1.93(3)	2.708(3)	165(3)	$1 - x, 1 - y, 2 - z$
O(9)-H(9B)···O(11)	0.83(3)	1.90(3)	2.730(3)	175(3)	$-1 + x, y, z$
O(11)-H(11A)···O(2)	0.79(4)	2.06(4)	2.821(3)	161(3)	$1 + x, y, z$
O(11)-H(11B)···O(4)	0.76(4)	2.12(4)	2.865(3)	169(4)	$1 - x, 1 - y, 2 - y$
O(12)-H(12A)···O(6)	0.77(3)	2.01(4)	2.768(3)	166(3)	
O(12)-H(12B)···O(11)	0.81(3)	1.99(3)	2.744(3)	156(3)	$2 - x, 1 - y, 1 - z$
N(2)-H(2)···O(12)	0.86	2.02	2.874(3)	170.8	$2 - x, - y, 1 - x$
2b					
O(7)-H(7A)···O(2)	0.87(3)	1.85(3)	2.699(3)	166(3)	$1 + x, y, z$
O(7)-H(7B)···O(8)	0.66(4)	2.04(4)	2.698(3)	175(4)	
O(8)-H(8A)···O(4)	0.80(3)	1.82(3)	2.606(3)	167(3)	$1 - x, 1 - y, 2 - z$
O(8)-H(8B)···O(12)	0.74(3)	2.07(3)	2.791(3)	168(4)	$1 - x, 1 - y, 1 - z$
O(9)-H(9A)···O(10)	0.79(4)	1.93(4)	2.703(3)	167(4)	$1 - x, 1 - y, 2 - z$
O(9)-H(9B)···O(11)	0.85(3)	1.88(3)	2.732(3)	174(3)	$-1 + x, y, z$
O(11)-H(11A)···O(2)	0.73(4)	2.12(4)	2.825(3)	161(4)	$1 + x, y, z$
O(11)-H(11B)···O(4)	0.82(4)	2.09(4)	2.893(3)	166(4)	$1 - x, 1 - y, 2 - y$
O(12)-H(12A)···O(6)	0.79(4)	1.99(4)	2.777(3)	170(4)	
O(12)-H(12B)···O(11)	0.76(4)	2.07(4)	2.774(3)	155(4)	$2 - x, 1 - y, 1 - z$
N(2)-H(2)···O(12)	0.86	2.02	2.880(3)	173.5	$2 - x, - y, 1 - x$
2c					
O(7)-H(7A)···O(2)	0.81(3)	1.88(3)	2.685(2)	173(3)	$1 + x, y, z$
O(7)-H(7B)···O(8)	0.77(3)	1.92(3)	2.685(2)	174(3)	
O(8)-H(8A)···O(4)	0.83(3)	1.80(3)	2.603(2)	162(2)	$1 - x, 1 - y, 2 - z$
O(8)-H(8B)···O(12)	0.79(3)	1.99(3)	2.766(2)	169(2)	$1 - x, 1 - y, 1 - z$

O(9)-H(9A)···O(10)	0.76(3)	1.96(3)	2.707(2)	170(3)	$1-x, 1-y, 2-z$
O(9)-H(9B)···O(11)	0.84(3)	1.90(3)	2.731(2)	174(2)	$-1+x, y, z$
O(11)-H(11A)···O(2)	0.80(3)	2.07(3)	2.818(2)	156(3)	$1+x, y, z$
O(11)-H(11B)···O(4)	0.78(3)	2.10(3)	2.863(2)	169(3)	$1-x, 1-y, 2-y$
O(12)-H(12A)···O(6)	0.75(3)	2.03(3)	2.770(2)	169(3)	
O(12)-H(12B)···O(11)	0.79(3)	1.99(3)	2.742(2)	157(3)	$2-x, 1-y, 1-z$
N(2)-H(2)···O(12)	0.86	2.02	2.876(2)	171.6	$2-x, -y, 1-x$

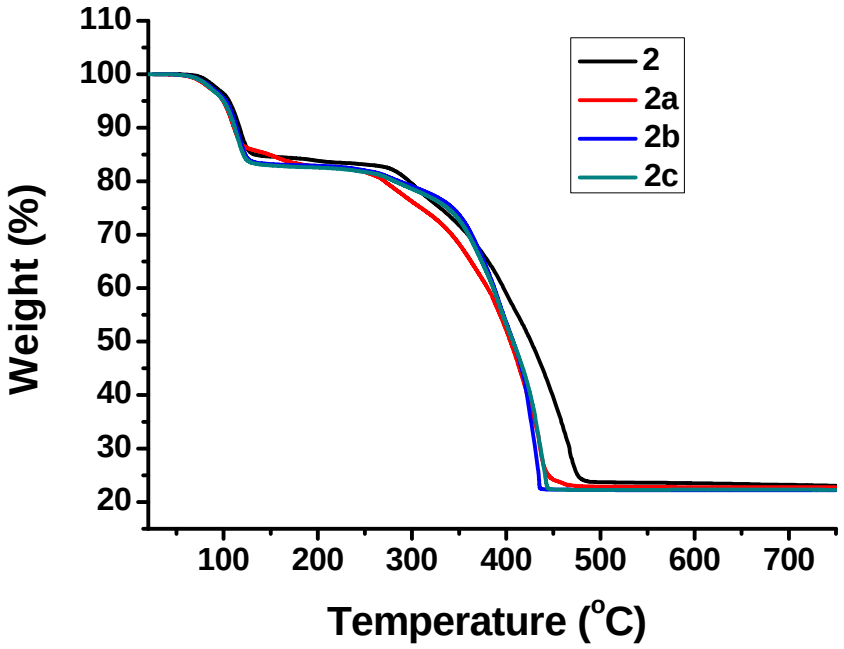


Fig. S1 The TGA curves for **2** and **2a**−**2c**.

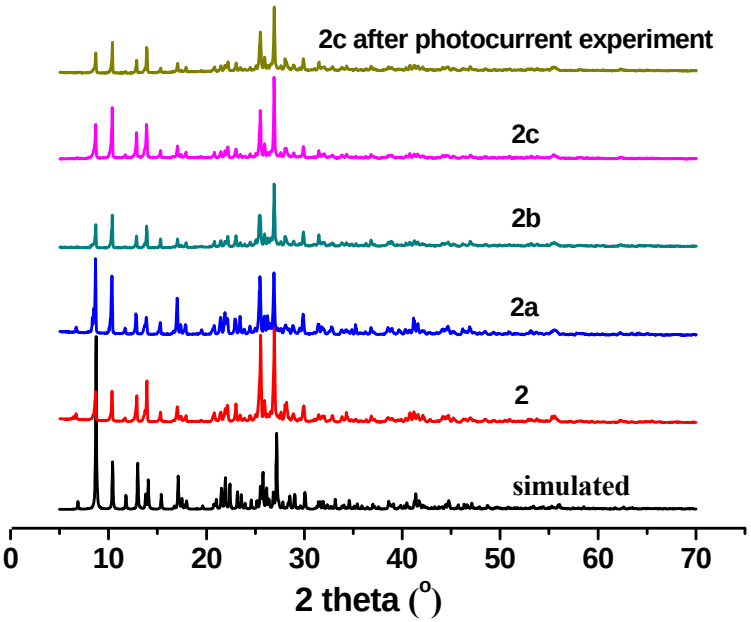


Fig. S2 The PXRD patterns of **2**, **2a**−**2c**.

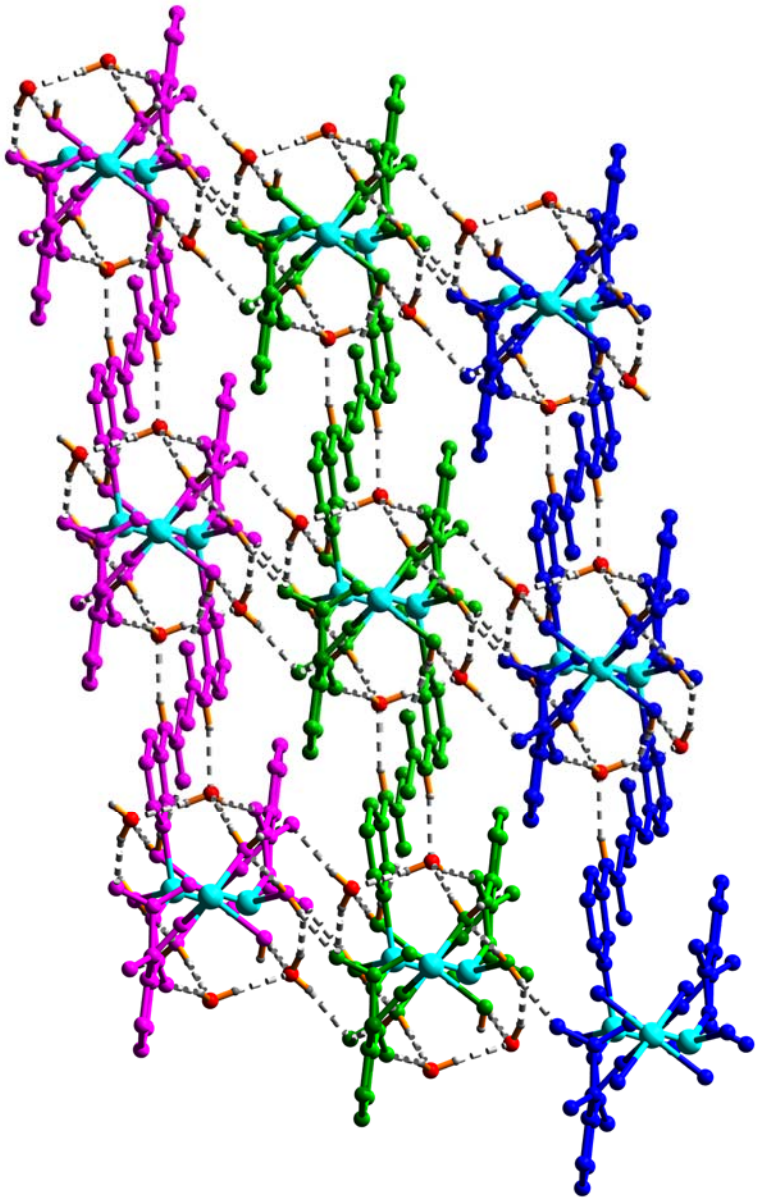
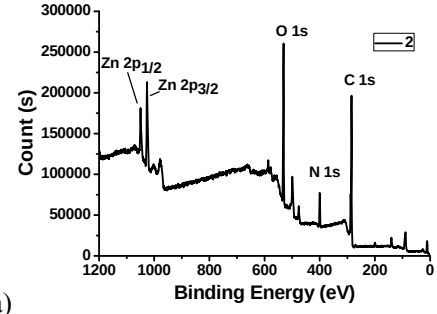
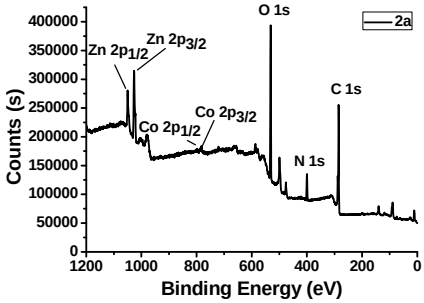


Fig. S3 View of the 3D hydrogen-bonded structure of **2** supported by H-bonds.

(a)


Count (s)
Binding Energy (eV)
Zn 2p1/2
Zn 2p3/2
O 1s
C 1s
N 1s
2


Counts (s)
Binding Energy (eV)
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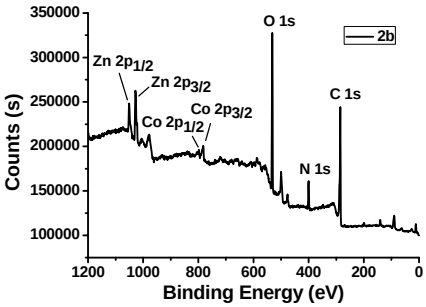
Zn 2p3/2
Co 2p1/2
Co 2p3/2
O 1s
C 1s
N 1s
2a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Binding Energy (eV)
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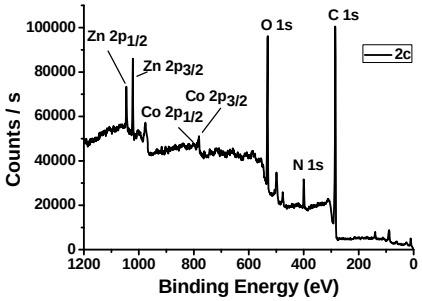
Zn 2p3/2
Co 2p1/2
Co 2p3/2
O 1s
C 1s
N 1s
2b


Counts / s
Binding Energy (eV)
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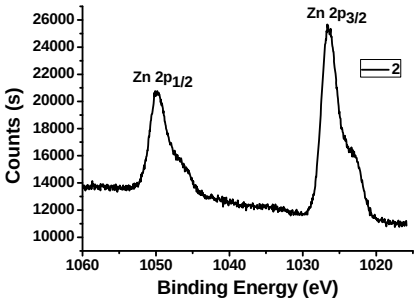
Zn 2p3/2
Co 2p1/2
Co 2p3/2
O 1s
C 1s
N 1s
2c

(b)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Binding Energy (eV)
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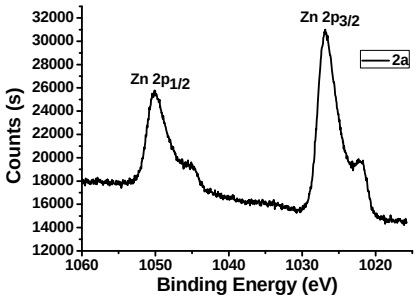
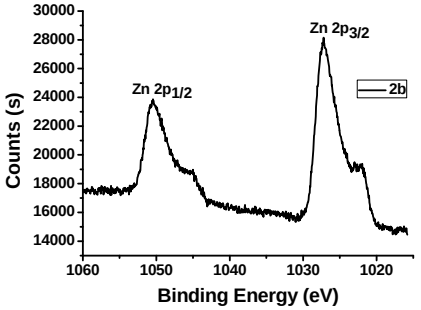
Zn 2p3/2
2


Counts (s)
Binding Energy (eV)
Zn 2p1/2
Zn 2p3/2
2a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Binding Energy (eV)
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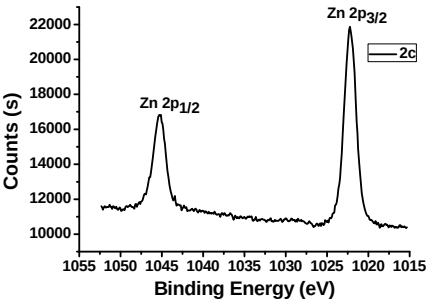
Zn 2p3/2
2b


Counts (s)
Binding Energy (eV)
Zn 2p1/2
Zn 2p3/2
2c

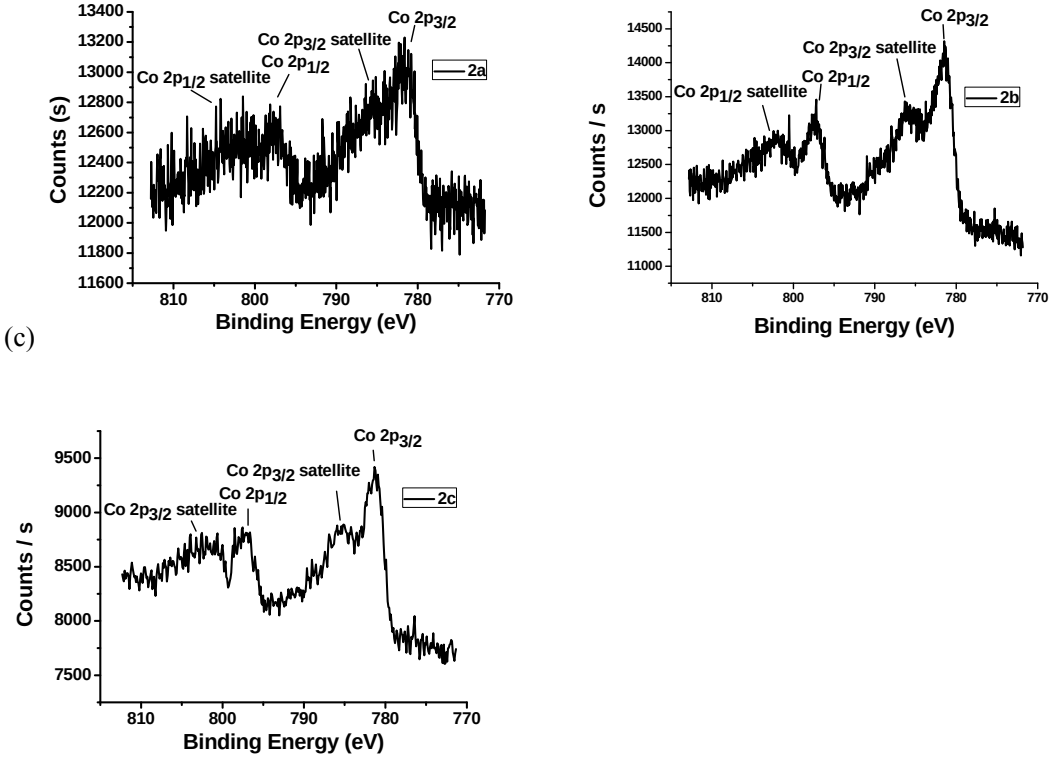


Fig. S4 XPS of **2**, **2a**−**2c** (a), Zn 2p (b) and Co 2p (c) regions of **2**, **2a**−**2c**.