Electronic Supporting Information

Reversible photo/thermal stimuli-responsive electrical bistability performances in supramolecular co-crystal accompanied by crystalline-to-amorphous transformations

Qian Liu, Liming Zhao, Wei Wu, Yan He, Kaiyue Song, Jiayuan Qi, Haohong Li*, Zhirong Chen*

College of chemistry, Fuzhou University, Fuzhou, Fujian, 350108, China

Table S1 Summary of the crystal data and structure determinations for co-crystal at room temperature and samples after heating/irradiating

	RT	Heated at 107℃	Heated at 110℃
Empirical formula	$C_{12}H_{24}N_{14}O_8$	$C_{12}H_{24}N_{14}O_8$	$C_{12}H_{24}N_{14}O_8$
Formula mass	492.45	492.45	492.45
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a[Å]	7.0700(12)	7.1278(15)	7.1004(10)
b[Å]	9.7833(16)	9.7918(11)	9.7553(13)
c [Å]	15.443(2)	15.501(2)	15.4226(18)
α[º]	101.117(3)	101.310(11)	101.355(10)
β[º]	100.009(2)	100.178(15)	100.201(11)
γ[º]	96.887(2)	96.415(13)	96.398(11)
V[Å]	1019.1(3)	1032.1(3)	1018.9(2)
Z	2	2	2
D_c[g/cm^3]	1.605	1.585	1.605
μ[mm^{-1}]	0.135	0.133	0.135
F(000)	516	516	516
Reflections, total	6356	17142	13211
Reflections, unique	3495 (R_{int}= 0.0207)	4802(R_{int}= 0.1317)	4686(R_{int}= 0.0960)
Reflections, observed	3030	1873	2027
Goodness-of-fit on F^2	1.052	0.923	1.017
No. of parameters refined	311	274	320
$R[I>2\sigma(I)]$	0.0345	0.0902	0.0783
R_w $[I>2\sigma(I)]$	0.1001	0.2241	0.1639
Residual extremes(e/Å^3)	0.241, -0.270	0.515, -0.491	0.677, -0.509

	Irradiating for 0.5 h	Irradiating for 1 h	Irradiating for 1.5 h
Empirical formula	$C_{12}H_{24}N_{14}O_8$	$C_{12}H_{24}N_{14}O_8$	$C_{12}H_{24}N_{14}O_8$
Formula mass	492.45	492.45	492.45
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a[Å]	7.1340(6)	7.1231(13)	7.1186(7)
b[Å]	9.8000(7)	9.7927(16)	9.7784(6)
c [Å]	15.5172(12)	15.574(3)	15.4920(12)
α[°]	101.331(6)	101.404(14)	101.367(6)
β[°]	100.248(7)	100.300(15)	100.201(7)
γ[°]	96.380(7)	96.379(15)	96.332(6)
V[Å]	1034.68(14)	1035.6(3)	1028.67(14)
Z	2	2	2
D_c[g/cm^3]	1.581	1.579	1.590
μ[mm^{-1}]	0.133	0.133	0.134
F(000)	516	516	516
Reflections, total	13573	14087	13950
Reflections, unique	4746(R_{int}= 0.0725)	3656(R_{int}= 0.0960)	4786(R_{int}= 0.0779)
Reflections, observed	2250	1318	2125
Goodness-of-fit on F^2	1.035	0.877	1.071
No. of parameters refined	289	308	319
R[I>2σ(I)]	0.0696	0.0940	0.0917
R_w [I>2σ(I)]	0.1523	0.2230	0.2622
Residual extremes(e/Å^3)	0.565,-0.473	0.488, -0.404	0.484, -0.398

Table S2 Hydrogen bridging details in co-crystal at room temperature

Type	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/°	Symmetry codes
MA^+–MA^+	N(3)–H(3A)···N(8)	0.86	2.19	3.0249(17)	164	-x,2-y,1-z
	N(7)–H(7B)···N(11)	0.86	2.40	3.259(2)	179	
	N(9)–H(9A)···N(6)	0.86	2.10	2.941(2)	167	
	N(14)–H(14A)···N(10)	0.86	2.18	3.0372(19)	177	1-x,-y,1-z
MA^+–$PZDC^{2-}$	N(3)–H(3B)···O(2)	0.86	2.32	3.0372(16)	141	1+x,y,z
	N(3)–H(3B)···O(4)	0.86	2.20	2.8365(16)	130	1+x,y,z
	N(4)–H(4)···O(2)	0.86	1.99	2.7797(15)	152	1+x,y,z
	N(7)–H(7A)···O(4)	0.86	2.04	2.8901(15)	170	-x,1-y,1-z
	N(12)–H(12A)···O(5)	0.86	1.94	2.7697(16)	162	-x,1-y,1-z
	N(12)–H(12B)···O(3)	0.86	2.48	3.1782(16)	139	-x,1-y,1-z
	N(13)–H(13)···O(3)	0.86	1.99	2.7972(16)	155	-x,1-y,1-z
MA^+–H_2O	N(5)–H(5A)···O(6)	0.86	2.19	3.0249(17)	164	1+x,y,z
	N(5)–H(5B)···O(8)	0.86	2.04	2.8493(19)	156	
	N(9)–H(9B)···O(6)	0.86	2.11	2.8767(18)	148	1+x,y,z
	N(12)–H(12B)···O(7)	0.86	2.48	3.0190(18)	122	-x,1-y,1-z
	N(14)–H(14B)···O(1)	0.86	2.23	2.9921(19)	148	1-x,-y,1-z

$PZDC^{2-}$–H_2O	O(1)–H(1A)···O(2)	0.89(3)	1.87(3)	2.7373(17)	163(2)	
	O(1)–H(1B)···O(3)	0.92(3)	1.97(3)	2.8533(17)	160(2)	1+x,y,z
	O(6)–H(6B)···O(5)	0.85	1.92	2.7620	168	
	O(7)–H(7C)···O(3)	0.85	2.15	3.0001	173	-x,1-y,2-z
	O(7)–H(7D)···N(2)	0.85	2.14	2.972(2)	167	
	O(8)–H(8A)···N(1)	0.85	2.12	2.934(2)	159	1-x,1-y,2-z
H_2O–H_2O	O(6)–H(6A)···O(1)	0.85	2.11	2.8758(17)	150	-1+x,y,z
	O(8)–H(8B)···O(7)	0.85	1.98	2.7990	161	

Table S3 Hydrogen bridging details of co-crystal heated at 110ºC

Type	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/º	Symmetry codes
MA^+–MA^+	N(3)–H(3A)···N(8)	0.86	2.18	3.038(8)	178	1-x,-y,1-z
	N(7)–H(7B)···N(13)	0.86	2.09	2.931(8)	167	1-x,1-y,1-z
	N(9)–H(9A)···N(11)	0.86	2.11	2.954(8)	169	2-x,-y,1-z
	N(12)–H(12A)···N(6)	0.86	2.36	3.223(8)	179	1-x,1-y,1-z
MA^+–$PZDC^{2-}$	N(4)–H(4)···O(2)	0.86	1.98	2.780(7)	155	1-x,-y,1-z
	N(5)–H(5A)···O(4)	0.86	1.92	2.750(8)	162	1-x,1-y,1-z
	N(5)–H(5B)···O(2)	0.86	2.48	3.171(8)	138	1-x,-y,1-z
	N(9)–H(9B)···O(3)	0.86	2.31	3.023(7)	141	2-x,-y,1-z
	N(9)–H(9B)···O(5)	0.86	2.18	2.820(8)	130	2-x,-y,1-z
	N(10)–H(10)···O(3)	0.86	1.96	2.752(8)	153	2-x,-y,1-z
	N(12)–H(12B)···O(5)	0.86	2.03	2.879(8)	169	
MA^+–H_2O	N(3)–H(3B)···O(6)	0.86	2.24	2.997(8)	147	
	N(5)–H(5B)···O(7)	0.86	2.48	3.033(8)	123	-1+x,y,z
	N(7)–H(7A)···O(1)	0.86	2.09	2.861(8)	148	
	N(14)–H(14A)···O(1)	0.86	2.19	3.023(9)	164	1-x,1-y,1-z
	N(14)–H(14B)···O(8)	0.86	2.05	2.849(8)	155	
$PZDC^{2-}$–H_2O	O(1)–H(1B)···O(4)	0.96(10)	1.87(10)	2.781(10)	157(8)	
	O(6)–H(6A)···O(3)	0.90(10)	1.87(9)	2.744(8)	64(8)	2-x,-y,1-z
	O(6)–H(6B)···O(2)	0.85(9)	2.13(10)	2.868(8)	145(9)	1-x,-y,1-z
	O(8)–H(8A)···N(1)	1.06	1.99	2.929(8)	145	-1+x,y,-1+z
H_2O–H_2O	O(1)–H(1A)···O(6)	0.60(11)	2.47(13)	2.878(9)	128(14)	1-x,-y,1-z
	O(7)–H(7C)···O(8)	0.88	2.53	2.940(9)	110	
	O(7)–H(7D) ···O(8)	1.06	2.55	2.940(9)	101	
	O(8)–H(8B)···O(7)	0.86	2.39	2.940(9)	122	

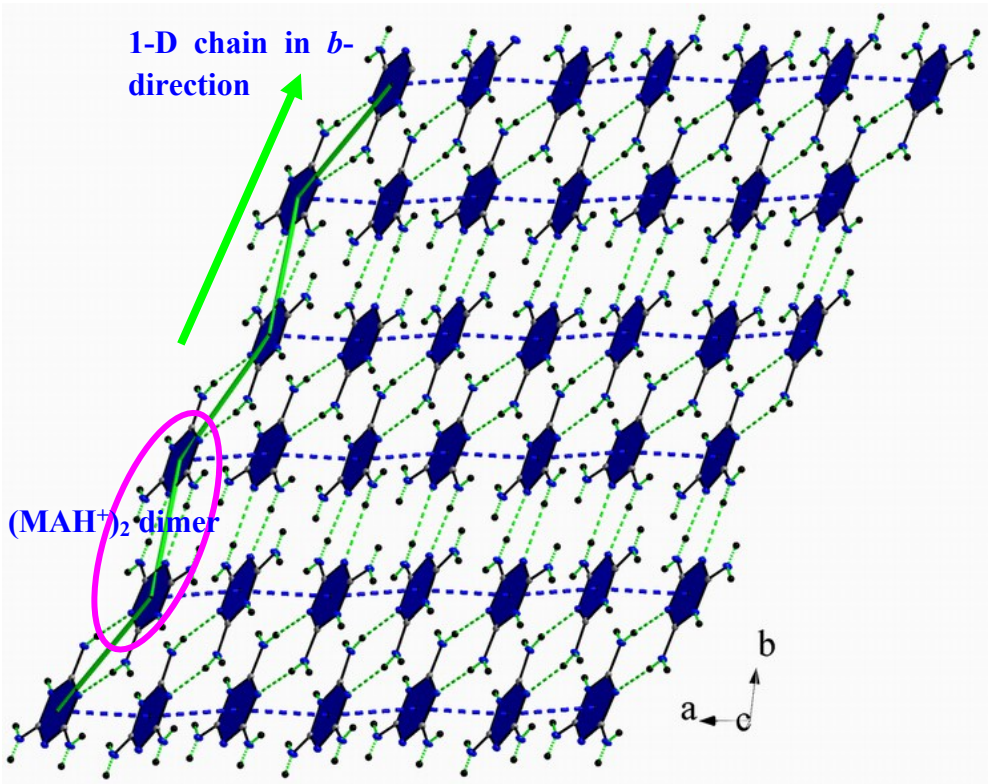
Table S4 Hydrogen bridging details of co-crystal after irradiating for 1 h

Type	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/º	Symmetry codes
MA^+–MA^+	N(3)–H(3A)···N(8)	0.86	2.19	3.053(7)	176	-x,1-y,-z
	N(7)–H(7A)···N(11)	0.86	2.10	2.948(7)	168	1-x,-y,-z

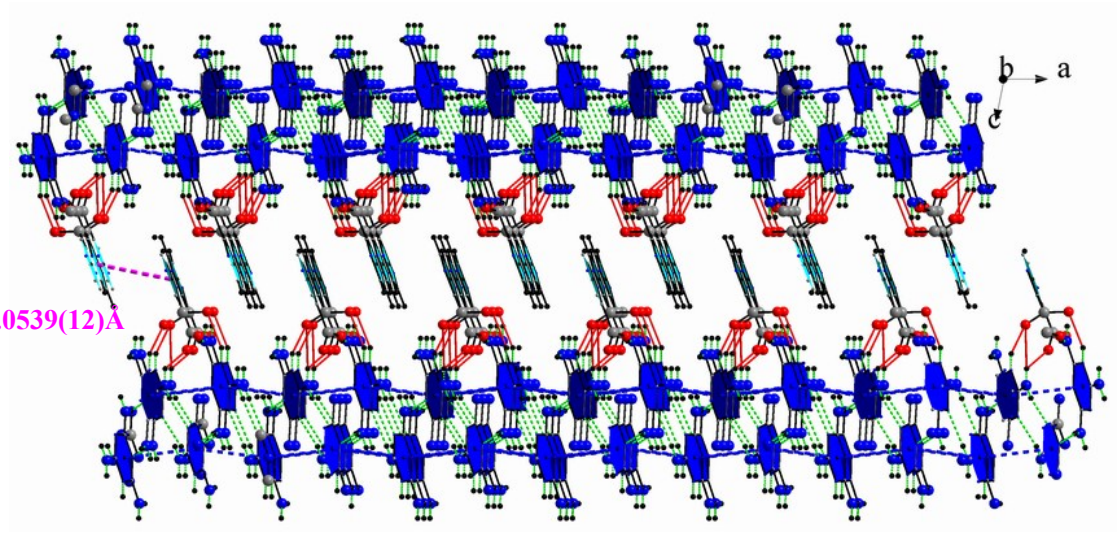
	N(9)–H(9A)···N(6)	0.86	2.39	3.255(8)	179	1-x,-y,-z
	N(14)–H(14A)···N(10)	0.86	2.14	2.988(7)	169	1-x,1-y,-z
MA^+–$PZDC^{2-}$	N(4)–H(4)···O(2)	0.86	1.97	2.778(8)	156	1-x,1-y,-z
	N(5)–H(5A)···O(5)	0.86	1.93	2.764(8)	164	1-x,-y,-z
	N(5)–H(5B)···O(2)	0.86	2.50	3.193(8)	139	1-x,1-y,-z
	N(9)–H(9B)···O(4)	0.86	2.06	2.909(9)	168	
	N(13)–H(13)···O(3)	0.86	1.98	2.785(7)	155	1-x,1-y,-z
	N(14)–H(14B)···O(3)	0.86	2.32	3.043(7)	141	1-x,1-y,-z
	N(14)–H(14B)···O(4)	0.86	2.19	2.828(8)	130	1-x,1-y,-z
MA^+–H_2O	N(3)–H(3B)···O(1)	0.86	2.26	3.025(8)	148	-x,1-y,-z
	N(5)–H(5B)···O(7)	0.86	2.52	3.065(10)	122	1-x,-y,-z
	N(7)–H(7B)···O(6)	0.86	2.12	2.881(8)	148	
	N(12)–H(12A)···O(6)	0.86	2.22	3.065(8)	167	1-x,-y,-z
	N(12)–H(12B)···O(8)	0.86	2.07	2.871(9)	154	
$PZDC^{2-}$–H_2O	O(1)–H(1A)···O(3)	1.09	1.77	2.748(8)	147	
	O(6)–H(6A)···O(5)	0.72	2.14	2.822(8)	156	-1+x,y,z
	O(6)–H(6B)···O(5)	0.84	2.50	2.822(8)	104	-1+x,y,z
	O(1)–H(1B)···O(2)	0.93	2.13	2.870(8)	136	-1+x,y,z
H_2O–H_2O	O(7)–H(7C)···O(8)	0.85	2.29	2.831(10)	122	1-x,-y,-z

Table S5 π–π stacking interactions of co-crystal at room temperature (lengths in Å and angles in °)

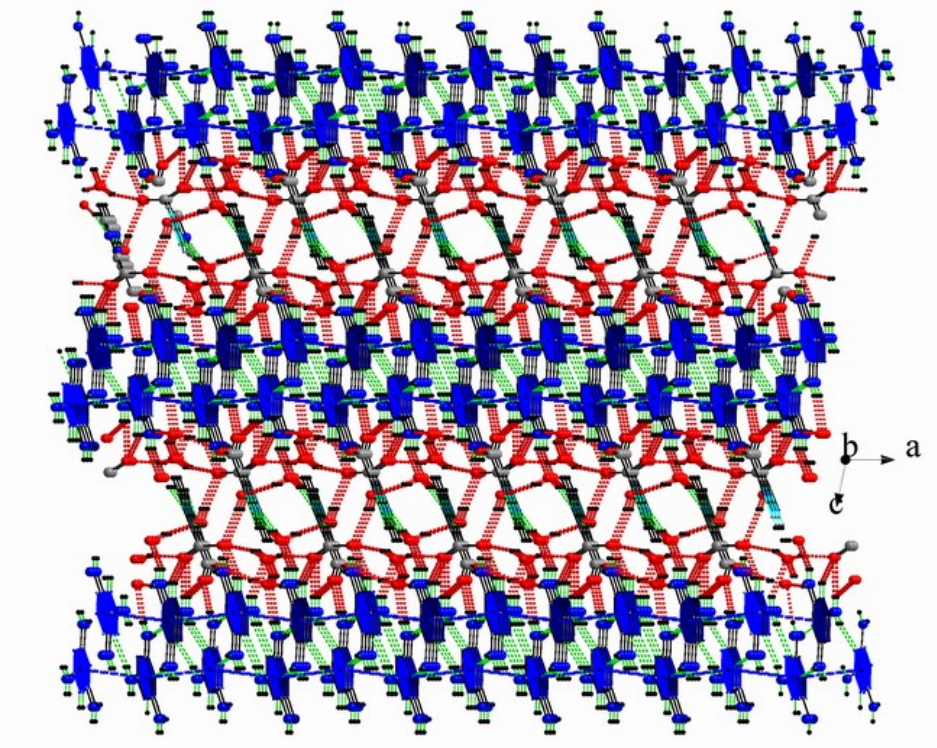
Cg(I)···Cg(J)	Symmetry code	Dist. Centroids	Dihedral angle	CgI_Perp dist.	CgJ_Perp dist.
Cg(1)→Cg(2)	1-x,1-y,1-z	3.5250(10)	4.08(7)	3.1874(6)	3.2541(6)
Cg(1): N(4)→C(11)→N(8)→C(10)→N(6)→C(12)→					
Cg(2): N(10)→C(8)→N(11)→C(7)→N(13)→C(9)→					



(a)

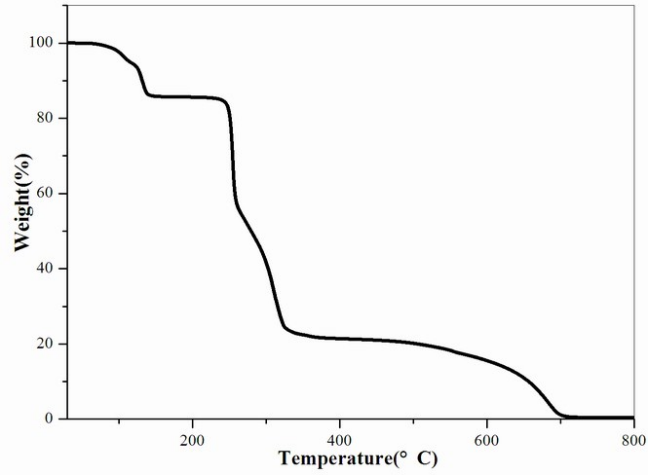


(b)



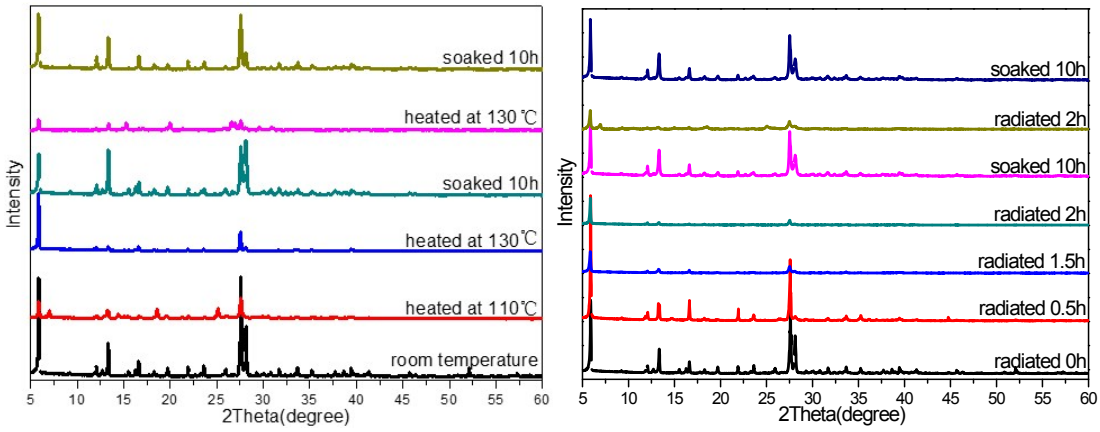
(c)

Fig. S1 (a) 2-D $(MAH)_{2n}^{2n+}$ layer constructed from hydrogen bonds (imaginary green line) and π···π stacking interactions (imaginary blue line); (b) the $(MA\text{-}H\cdot PZDC)_n$ layer showing the centroid distances between pyrazine rings without lattice waters; (c) 3-D network based on hydrogen bonds among $(MA\text{-}H\cdot PZDC)_n$ layers and lattice waters



(a)

(b)



(c) **(d)**

Fig. S2 (a) TGA curve; (b) diffraction patterns of sample at 120 ºC under X-ray single diffractometer; (c) XRD patterns of co-crystal with another two runs for different temperatures experiments; (d) XRD patterns of co-crystal with another two runs for irradiation experiments

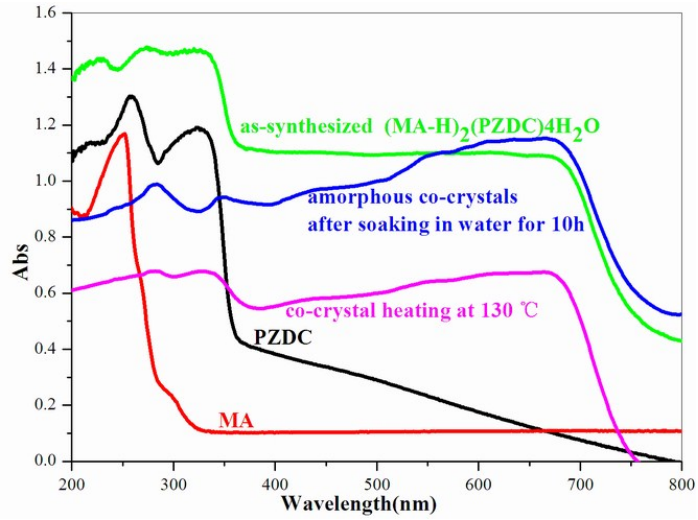
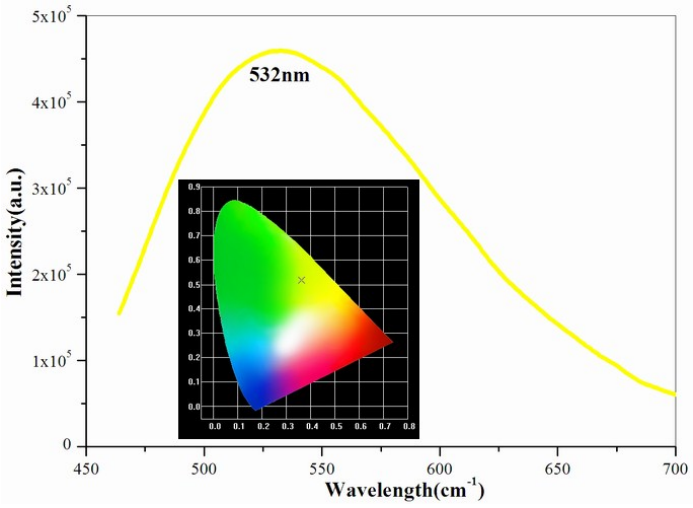
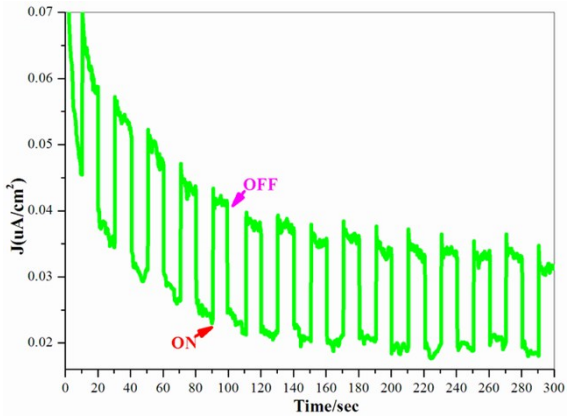


Fig. S3 UV-Vis spectra of MA, PZDC, as-synthesized (MA-H)$_2$(PZDC)·4H$_2$O co-crystal, co-crystals heated at 130 ºC and amorphous powders soaking in water for 10h

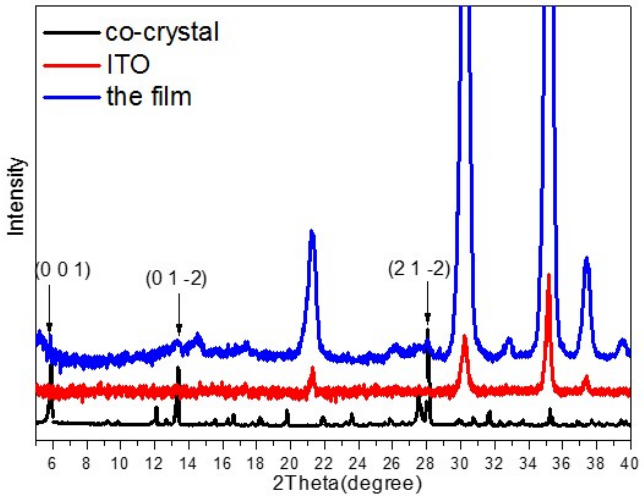


(a)

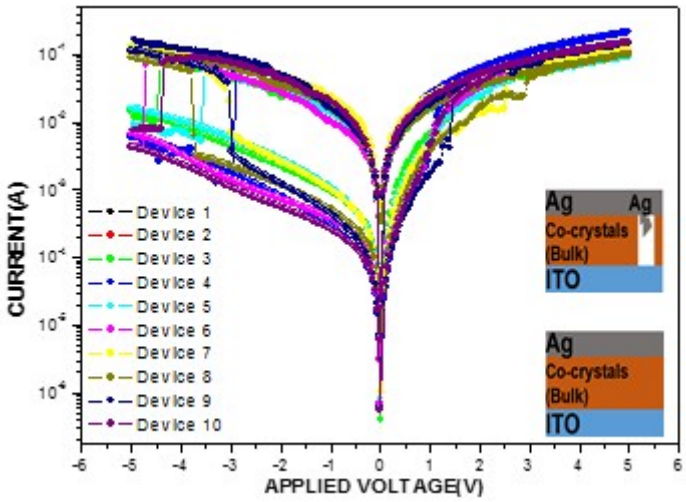


(b)

Fig. S4 (a) Solid- state emission spectra of co-crystal at room temperature; (b) I-T curve with on-off model

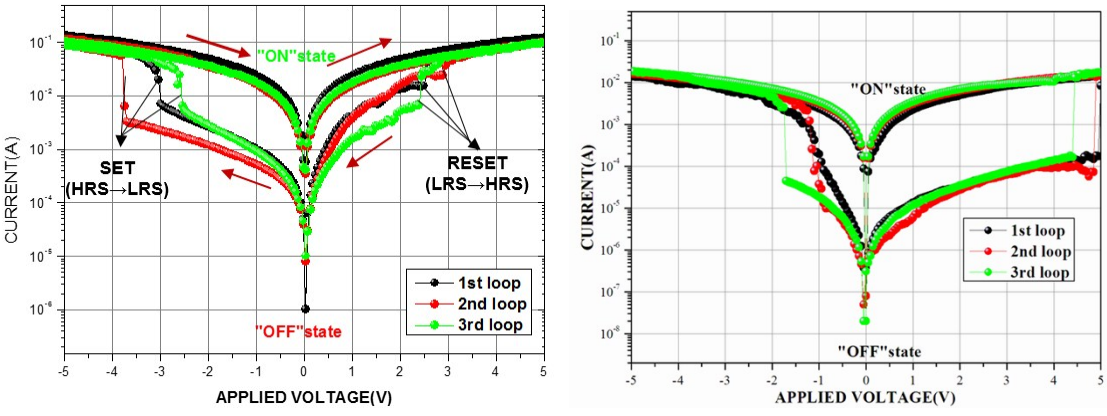


(a)

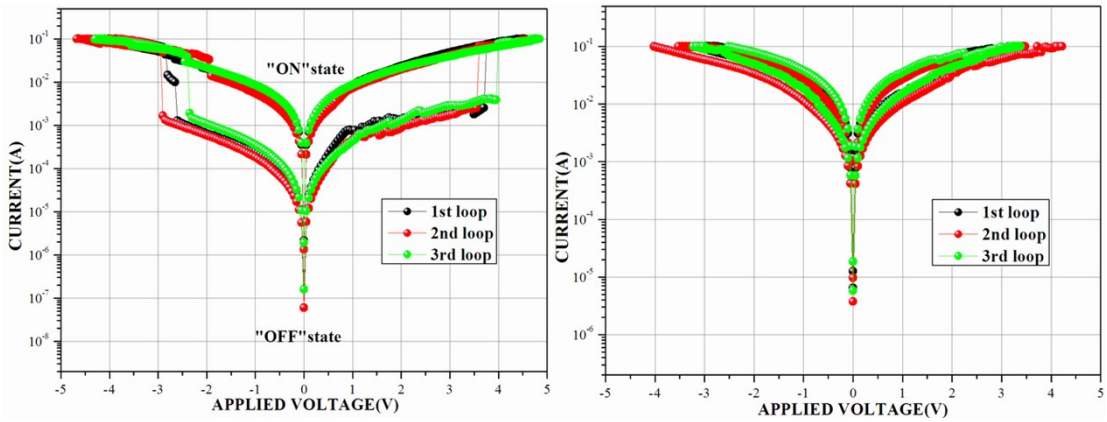


(b)

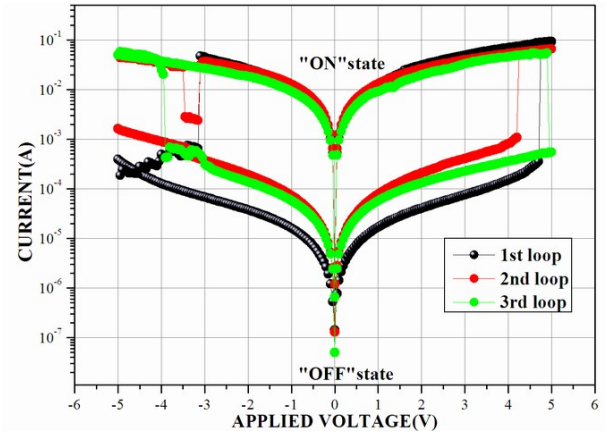
Fig. S5 (a) PXRD patterns of ITO/co-crystal film and ITO; (b) I-V curves of ten ITO/(MA-H)$_2$(PZDC)·4H$_2$O/Ag devices measured at room temperature



(a) **(b)**

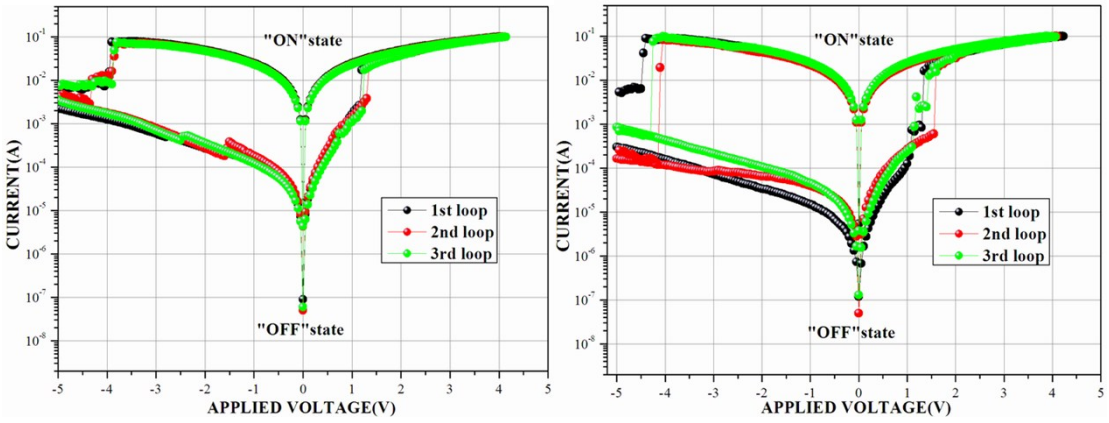


(c) **(d)**

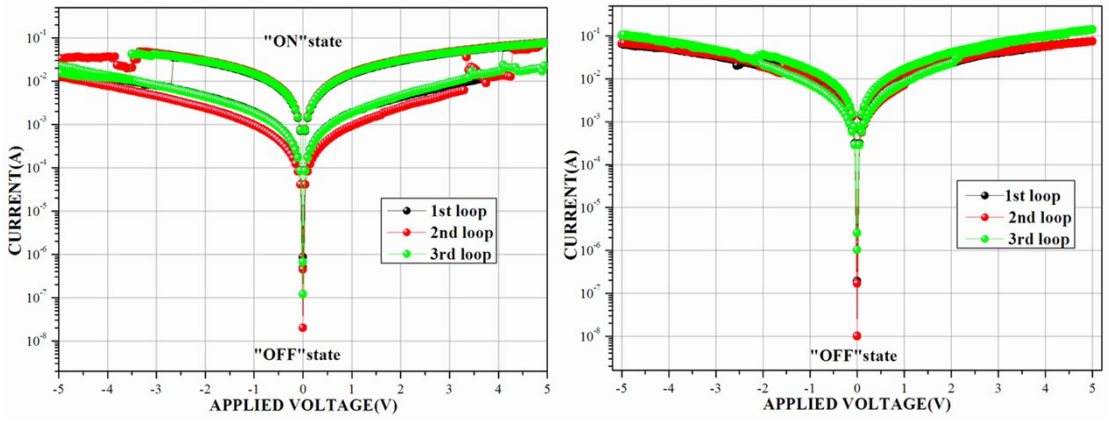


(e)

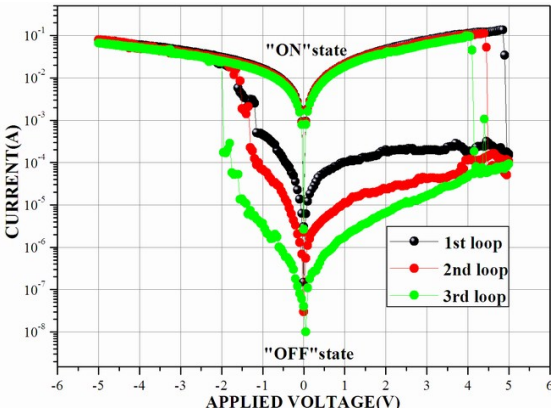
Fig. S6 I-V characteristics of ITO/(MA-H)$_2$(PZDC)·4H$_2$O/Ag device with three sweep cycles: (a) at room temperature; (b) heating at 107 ºC; (c) heating at 110 ºC; (d) heating at 130 ºC; (e) the recovery device after soaked in water for 10 h



(a) (b)

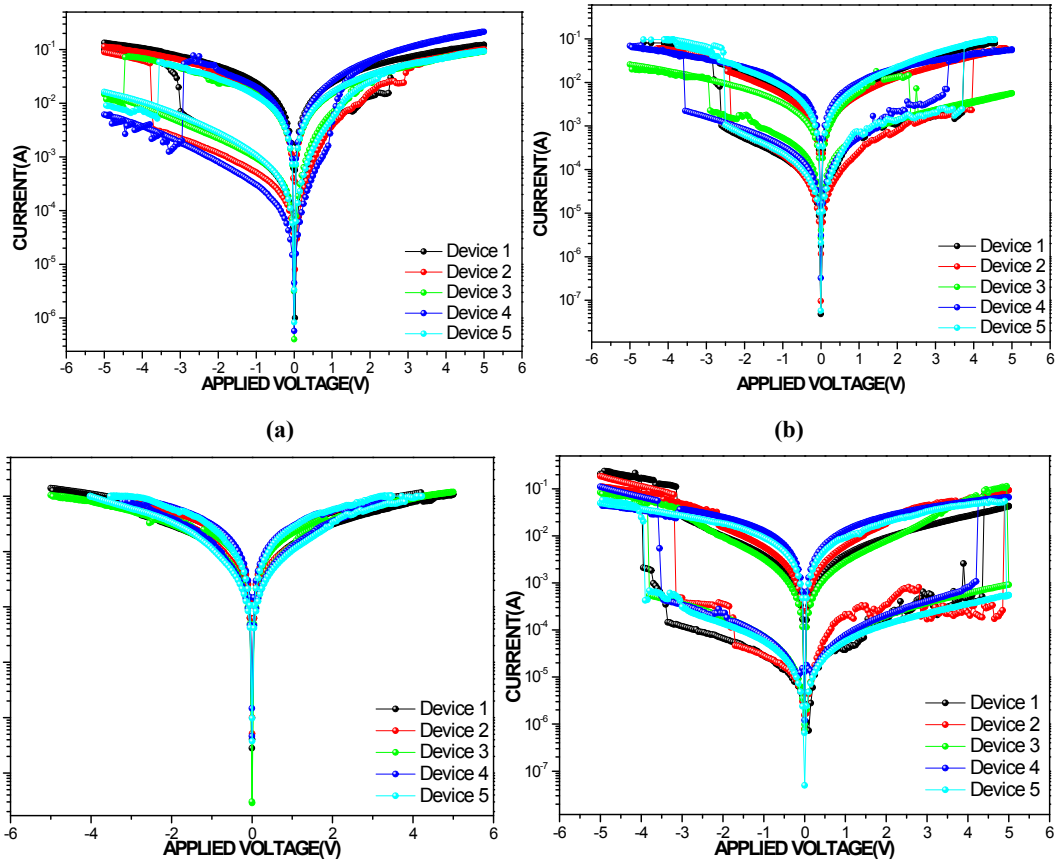


(c) (d)



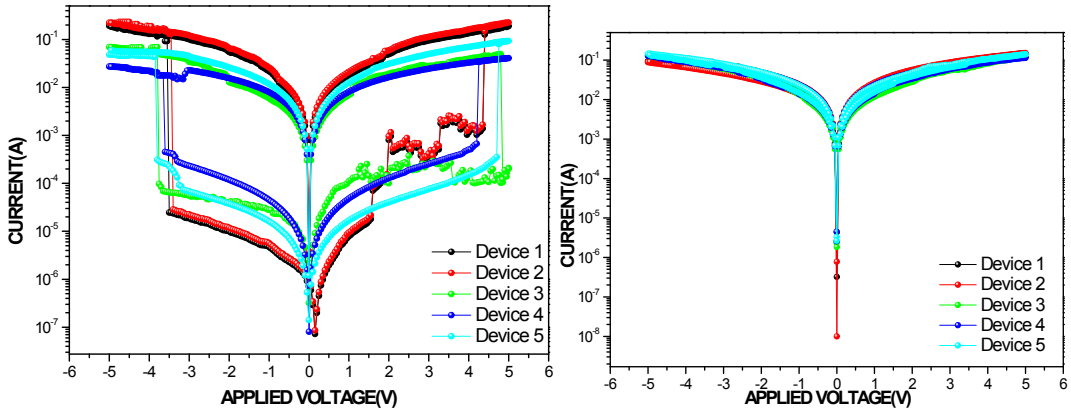
(e)

Fig. S7 I-V characteristics of ITO/$(MA\text{-}H)_2(PZDC)\cdot 4H_2O$/Ag device with three sweep cycles: (a) irradiating for 0.5h; (b) irradiating for 1h; (c) irradiating for 1.5h; (d) irradiating for 2h; (e) the recovery device after soaked in water for 10 h



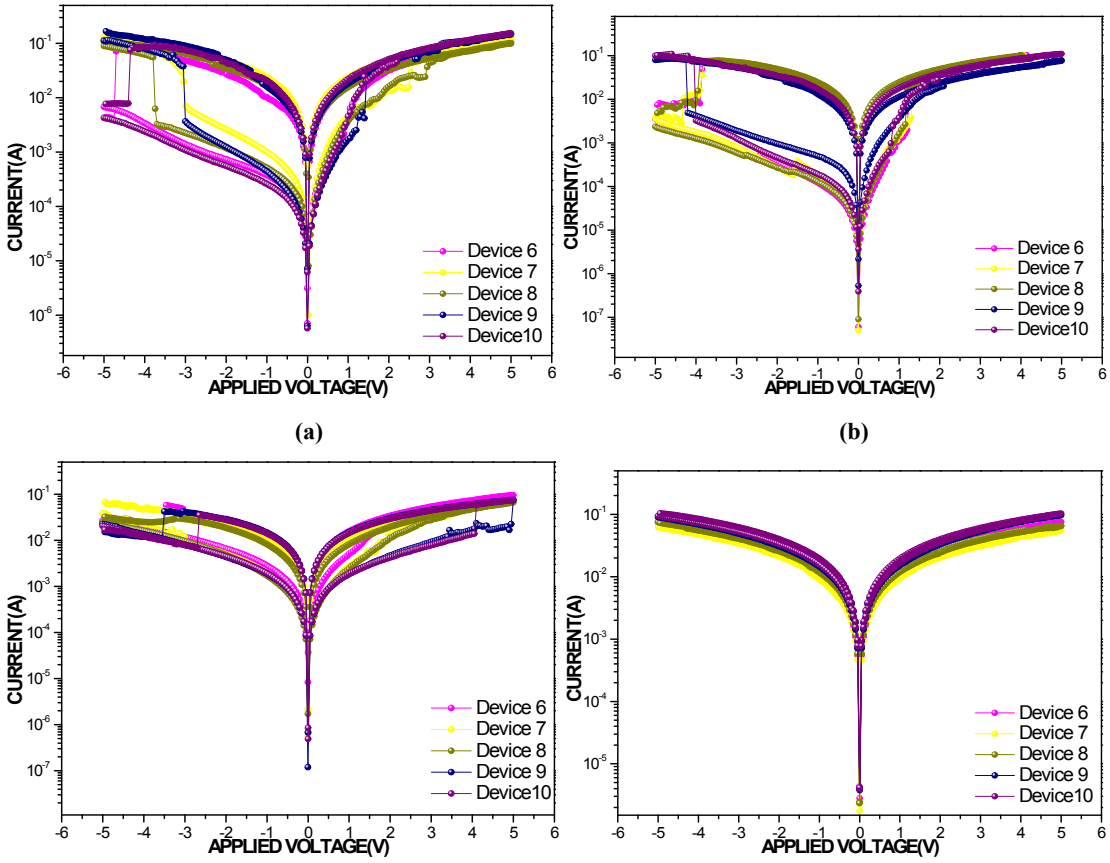
(a) (b)

(c) (d)



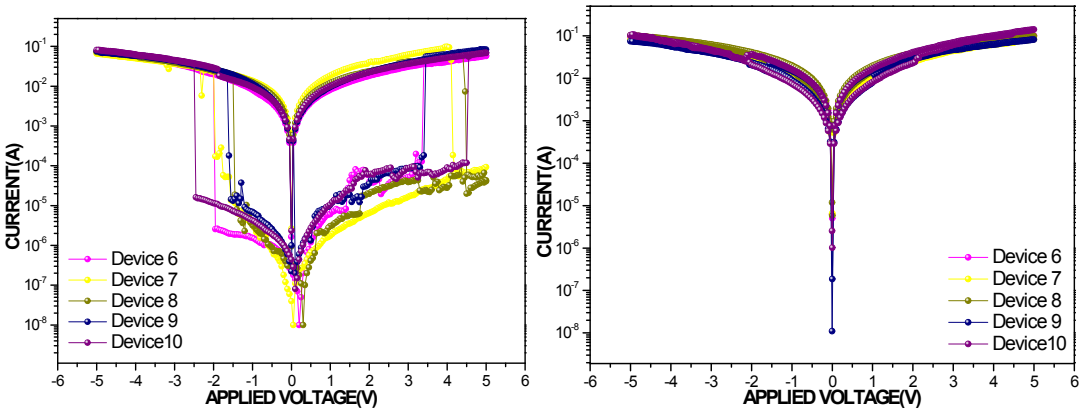
(e) (f)

Fig. S8 I-V characteristics of 5 ITO/$(MA\text{-}H)_2(PZDC)\cdot 4H_2O$/Ag devices with two runs for different temperatures experiment: the first run (a) at room temperature; (b) heating at 110 ºC; (c) heating at 130 ºC;(d) the recovery device after soaked in water for 10 h; the second run (e) heating at 130 ºC (f)

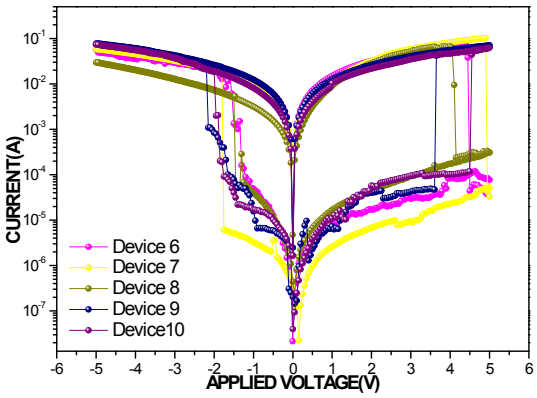


(a) (b)

(c) (d)

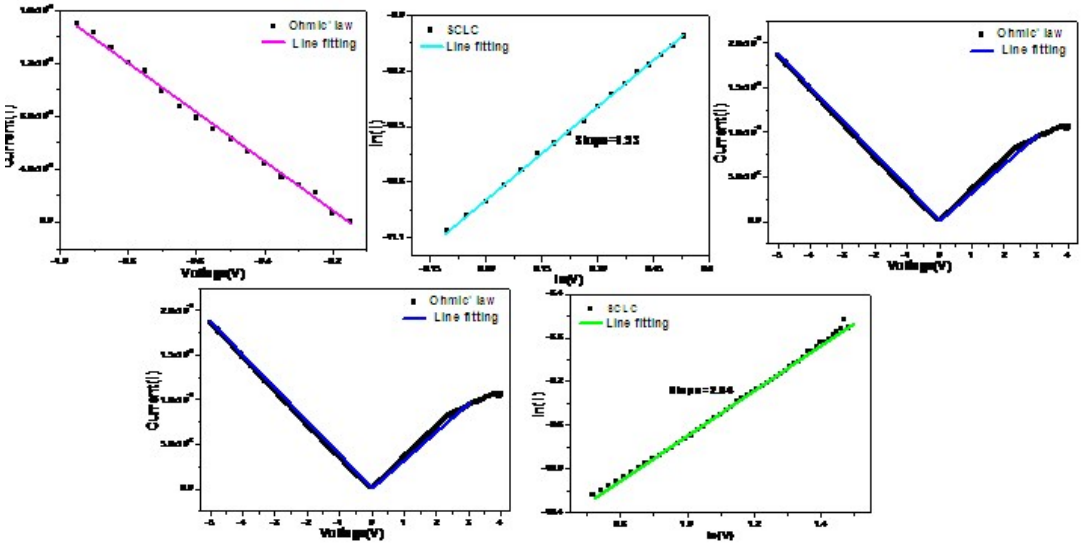


(e) (f)

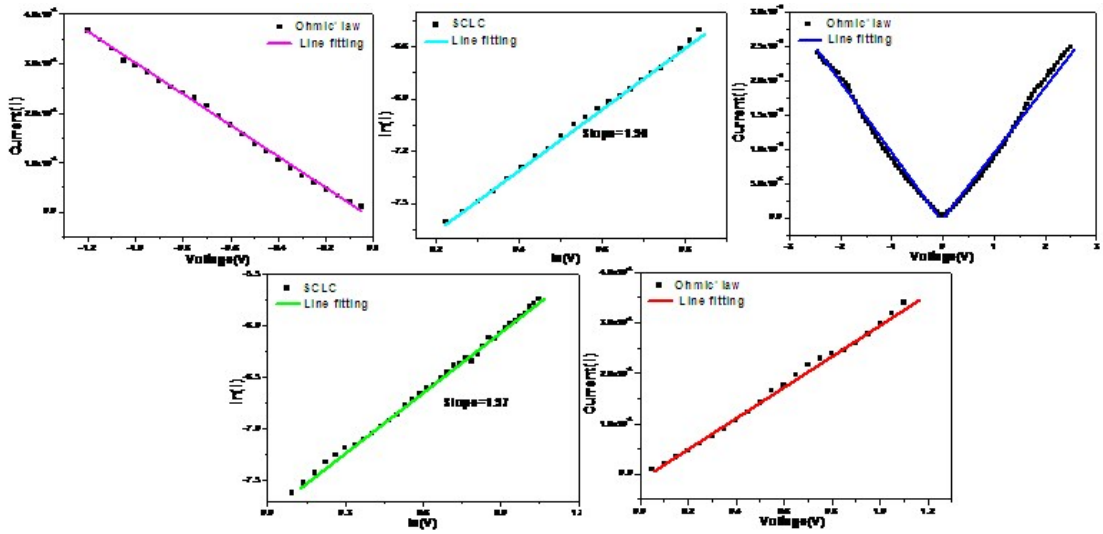


(g)

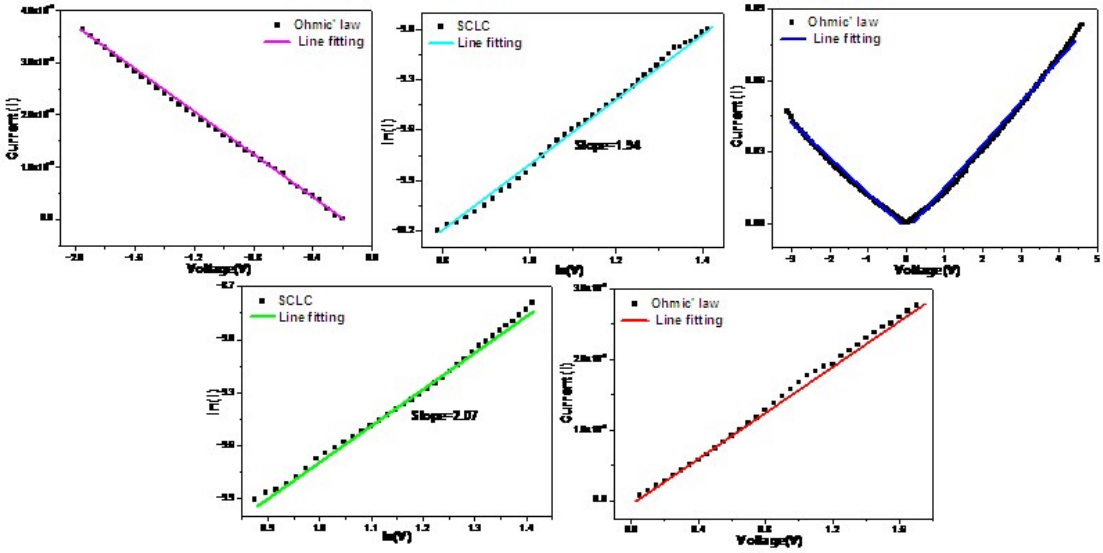
Fig. S9 I-V characteristics of five ITO/(MA-H)$_2$(PZDC)·4H$_2$O/Ag devices with two runs for different irradiation experiment: the first run (a) irradiating for 0h; (b) irradiating for 0.5h; (c) irradiating for 1.5h; (d) irradiating for 2h; (e) the recovery device after soaked in water for 10 h; the second run (f) irradiating for 2h; (g)the recovery device after soaked in water for 10 h



(a)

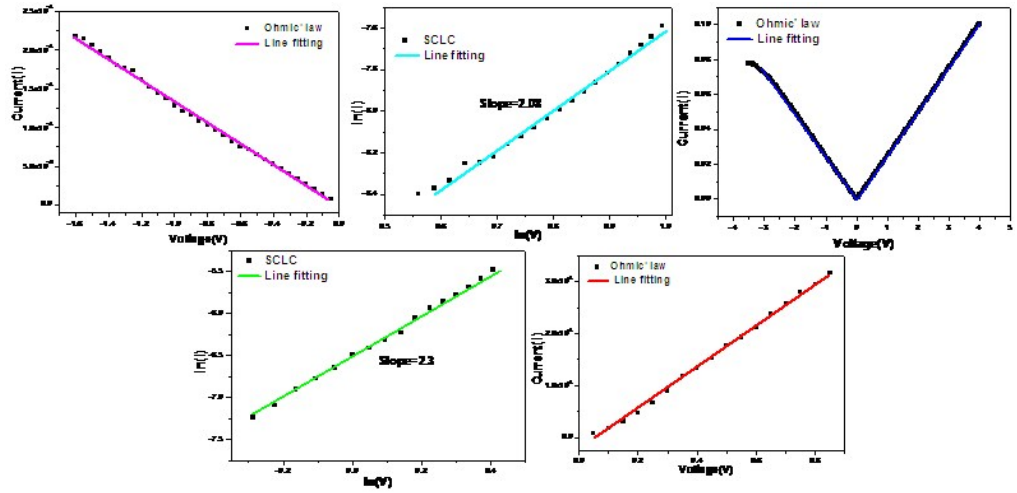


(b)

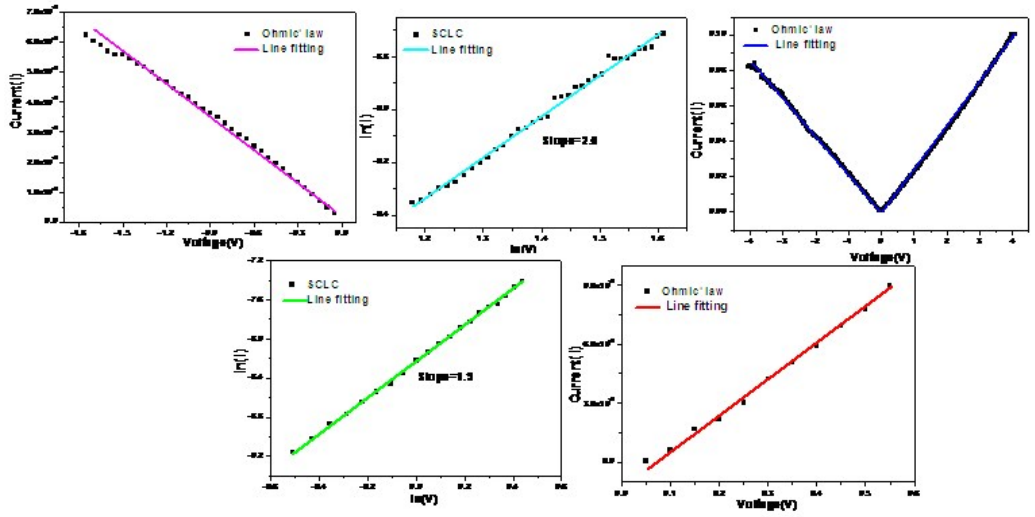


(c)

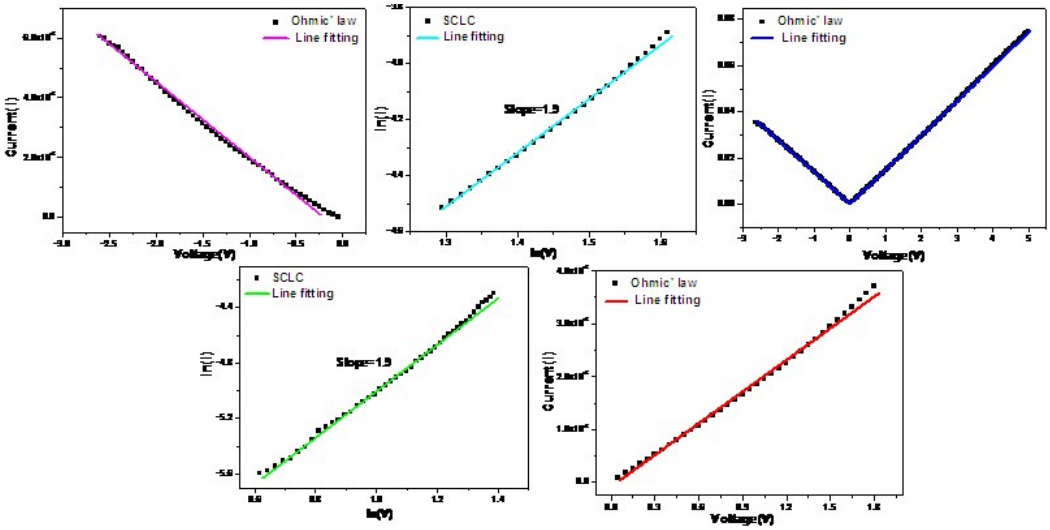
Fig. S10 Conduction mechanisms of thermally responsive ITO/co-crystal layer/Ag devices: (a) at 107 ℃: (b) at 110 ℃: (c) recovered device after soaking in water for 10h



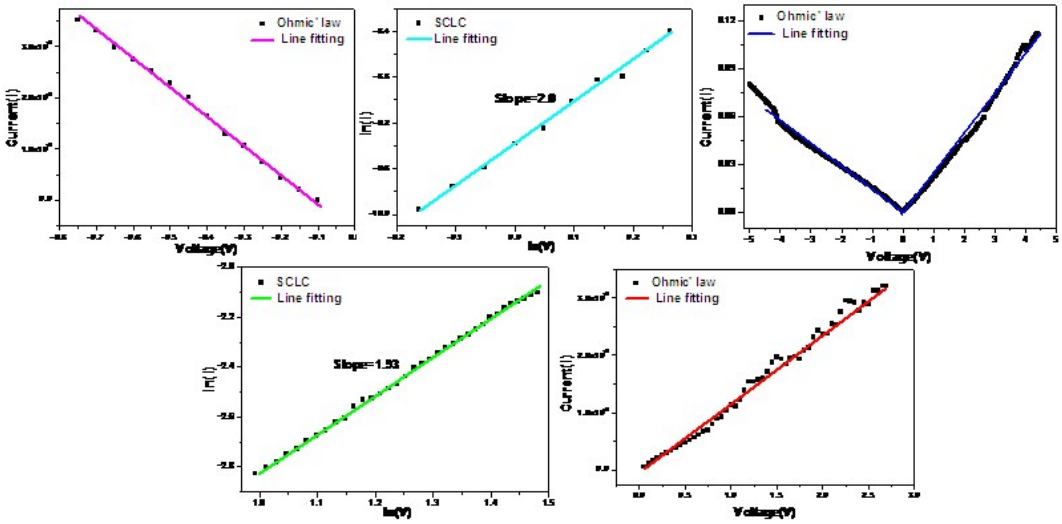
(a)



(b)



(c)



(d)

Fig. S11 Conduction mechanisms of photo responsive ITO/co-crystal layer/Ag devices: (a) irradiating for 30min: (b) irradiating for 60 min: (c) irradiating for 90 min: (d) recovered device after soaking in water for

10h

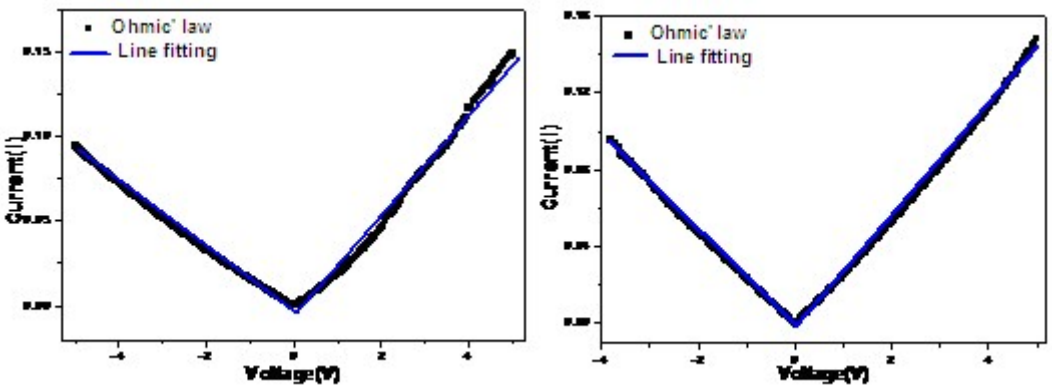
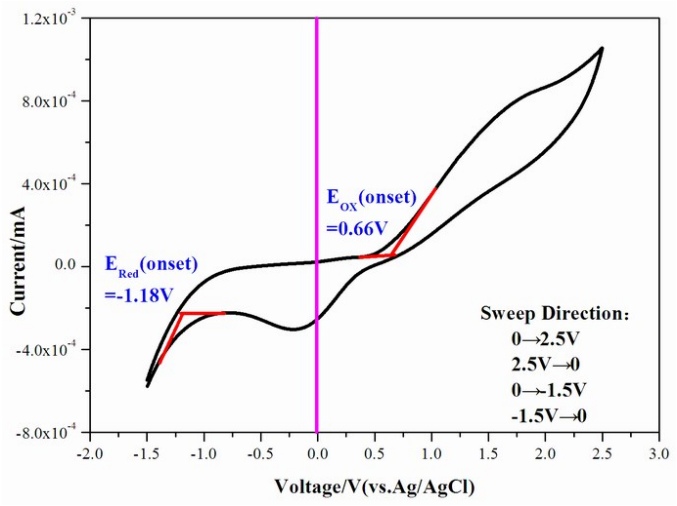
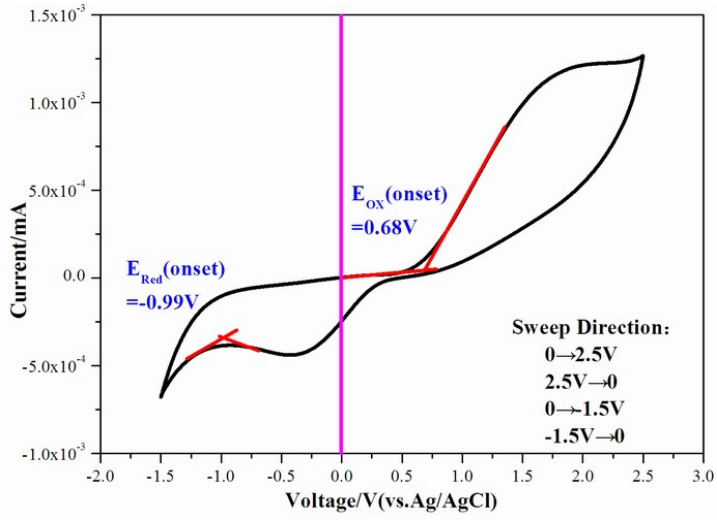


Fig. S12 I-V fitting of amorphous ITO/co-crystal layer/Ag device



(a)



(b)

Fig. S13 $E_{ox(onset)}$ and $E_{red(onset)}$ calculated from CV diagram in 0.1 M *n*-Bu_4BF_4 (scan rate: 0.1 V·S^{-1}): (a) initial co-crystal; (b) heated co-crystal