Supporting Information

Zero-Dimensional Hybrid Copper(I) Bromide Single Crystal with Highly Efficient Green Emission

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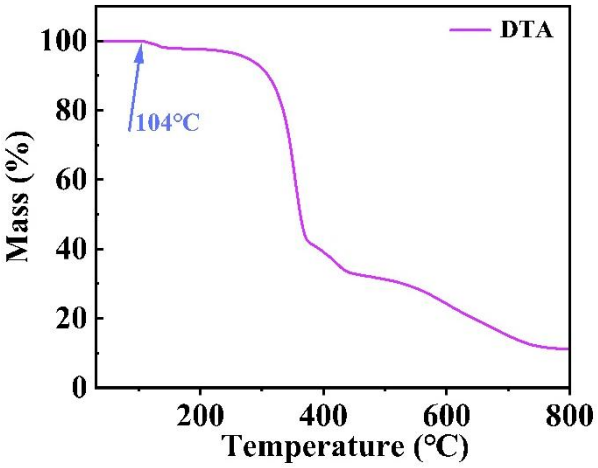

Figure S1. Thermogravimetric (TG) analysis $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$.

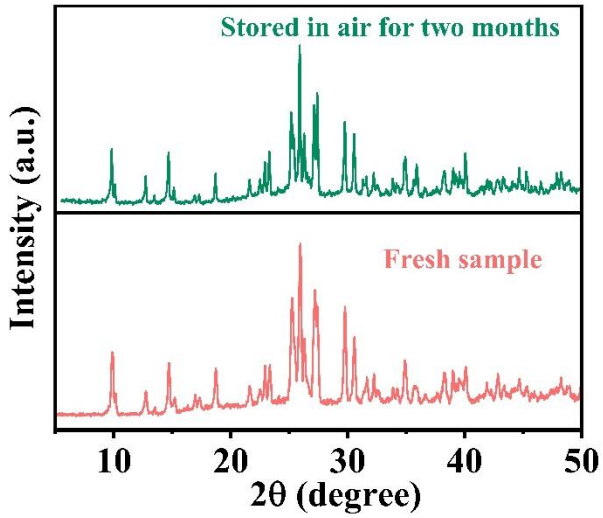

Figure S2. PXRD patterns of (AEP)2Cu2Br6·2Br·2H2O after the storage in air for two months.

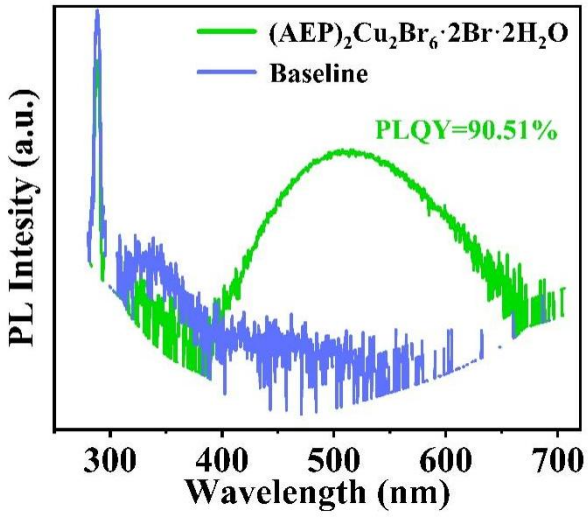

Figure S3. PLQY of $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$.

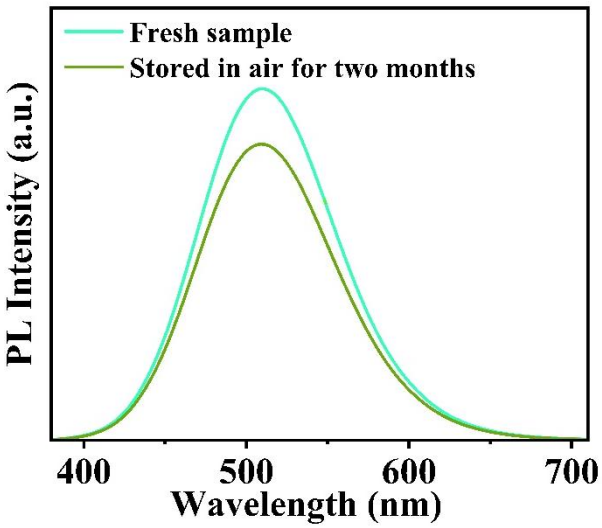

Figure S4. PL spectrum of $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$ after the storage in air for two months.

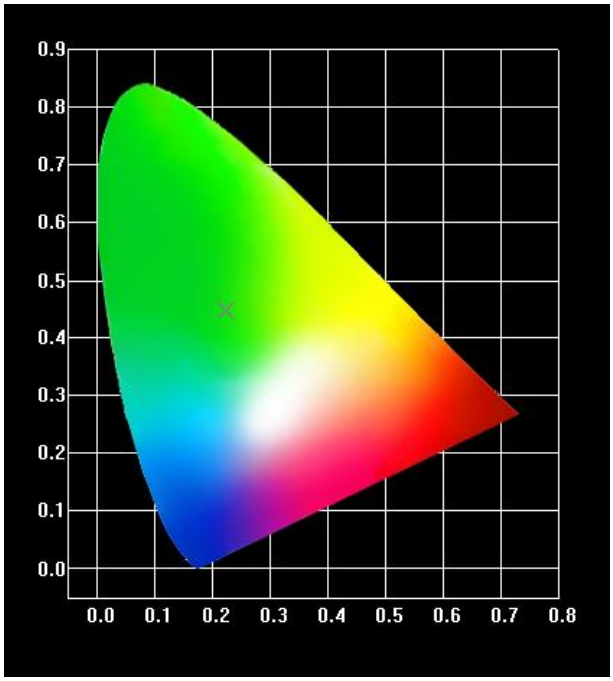

Figure S5. CIE chromaticity diagram of $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$.

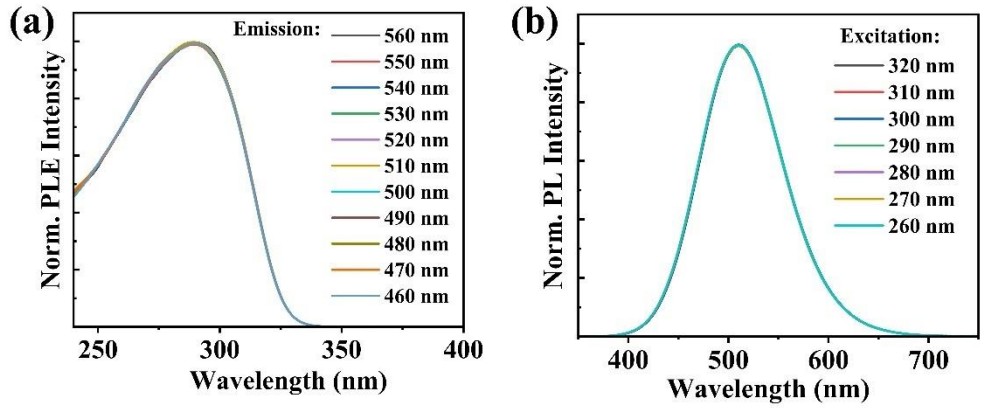

Figure S6. Wavelength-dependent PLE spectra and PL spectra.

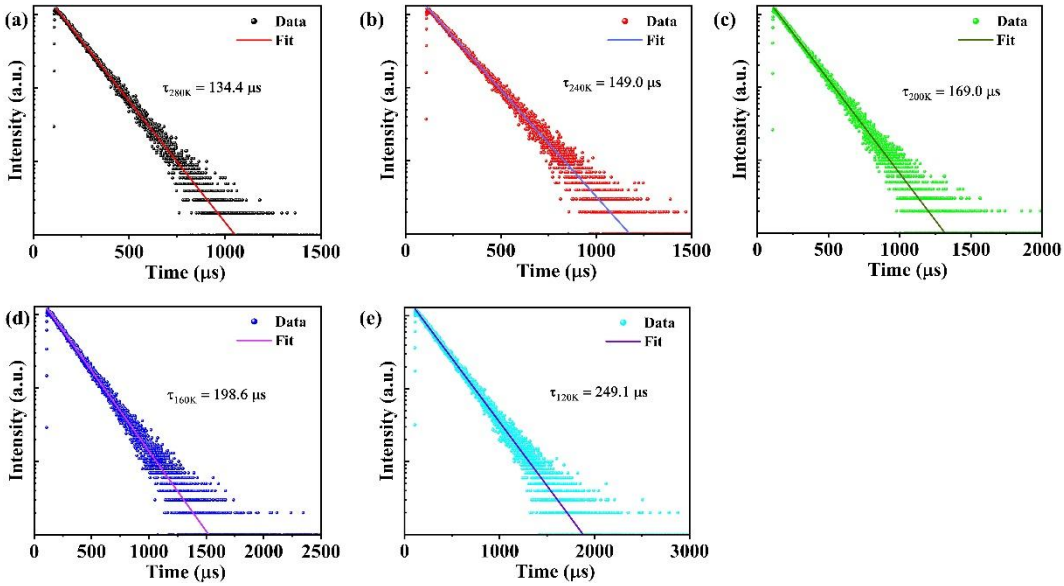

Figure S7. PL decay lifetime curves of the $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$ at 120-280K.

Table S1. Crystal data and structure refinement for $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$

Empirical formula	$C_{12}H_{40}Br_8Cu_2N_6O_2$
Formula weight	1066.86
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.85500(10)
b/Å	11.8895(2)
c/Å	14.0612(2)
α/°	90
β/°	97.6360(10)
γ/°	90
Volume/Å^3	1467.26(4)
Z	2
ρ_{calc}g/cm^3	2.415
μ/mm^{-1}	14.734
F(000)	1016.0
Crystal size/mm^3	8.855 × 14.0612 × 11.8895
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.778 to 152.952
Index ranges	$-9 \le h \le 11$, $-14 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	9870
Independent reflections	2969 [R_{int} = 0.0724, R_{sigma} = 0.0529]
Data/restraints/parameters	2969/0/141
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0632, wR_2 = 0.1661
Final R indexes [all data]	R_1 = 0.0655, wR_2 = 0.1769
Largest diff. peak/hole / e Å^{-3}	1.54/-1.81

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Br1	6852.8(6)	5144.3(4)	6020.3(4)	28.4(3)
Br3	4571.9(6)	8003.0(4)	4767.8(4)	31.1(3)
Br4	10872.4(7)	4210.0(5)	8919.4(4)	38.3(3)
N2	1827(5)	2981(3)	6977(3)	21.4(8)
O1	7337(5)	5138(4)	8861(3)	42.2(10)
N3	4463(5)	4418(4)	8172(3)	33.9(10)
N1	-754(5)	2570(4)	5508(3)	32.8(10)
C5	3330(6)	2604(4)	7521(4)	28.4(10)
C3	1926(6)	3148(4)	5930(3)	27.3(10)
C1	-883(6)	2411(5)	6550(4)	31.9(11)
C2	616(6)	2113(4)	7102(4)	30.9(11)
C6	4620(6)	3433(4)	7549(4)	29.6(10)
C4	398(6)	3460(5)	5390(4)	31.3(11)
Br2	2508.6(7)	6071.3(5)	6549.3(4)	32.7(3)
Cu1	4398.7(11)	6050.5(7)	5355.5(7)	40.7(3

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	38.1(4)	21.2(4)	25.5(4)	-4.26(17)	2.7(3)	0.72(19)
Br3	37.7(4)	24.2(4)	31.1(4)	-2.65(19)	3.1(3)	-1.75(19)
Br4	44.4(5)	40.8(4)	30.4(4)	-4.8(2)	7.6(3)	4.2(2)
N2	29.5(19)	13.2(17)	21(2)	1.2(14)	0.9(16)	0.0(14)
O1	40(2)	49(3)	36(2)	0.1(19)	0.2(18)	-6.4(19)
N3	38(2)	25(2)	35(2)	0.5(18)	-6(2)	-4.0(19)
N1	31(2)	42(3)	25(2)	2.1(19)	-1.2(17)	-2.1(19)
C5	39(2)	20(2)	26(2)	2.4(18)	1(2)	2(2)
C3	39(3)	23(2)	19(2)	5.7(17)	-2(2)	-5.5(19)
C1	30(2)	35(3)	31(3)	2(2)	7(2)	0(2)
C2	41(3)	22(2)	29(3)	5.3(19)	2(2)	-7(2)
C6	30(2)	29(3)	30(3)	3(2)	2(2)	-1(2)
C4	31(2)	37(3)	25(2)	12(2)	-2(2)	1(2)
Br2	40.6(4)	36.3(4)	21.3(4)	-0.23(19)	5.1(3)	7.5(2)
Cu1	48.7(6)	35.6(5)	37.8(6)	-2.4(3)	5.3(4)	1.8(4)

Table S4. Bond Lengths for $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu1	2.4934(11)	N1	C1	1.497(6)
Br1	Cu1[1]	2.5336(10)	N1	C4	1.494(7)
Br3	Cu1	2.4756(10)	C5	C6	1.505(7)
N2	C5	1.512(6)	C3	C4	1.508(7)
N2	C3	1.499(6)	C1	C2	1.489(7)
N2	C2	1.514(6)	Br2	Cu1	2.5232(11)
N3	C6	1.480(7)			

[1]1−X, 1−Y, 1−Z

Table S5. Bond Angles for $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu1	Br1	Cu1[1]	71.64(4)	N3	C6	C5	113.7(4)
C5	N2	C2	109.2(4)	N1	C4	C3	110.5(4)
C3	N2	C5	111.9(4)	Br1	Cu1	Br1[1]	108.36(4)
C3	N2	C2	109.8(4)	Br1	Cu1	Br2	112.14(4)
C4	N1	C1	109.9(4)	Br3	Cu1	Br1[1]	108.12(4)
C6	C5	N2	115.7(4)	Br3	Cu1	Br1	116.16(4)
N2	C3	C4	111.2(4)	Br3	Cu1	Br2	106.79(4)
C2	C1	N1	111.2(4)	Br2	Cu1	Br1[1]	104.59(4)
C1	C2	N2	111.9(4)				

[1]1−X, 1−Y, 1−Z

Table S6. Torsion Angles for $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	C5	C6	N3	72.0(6)	C3	N2	C2	C1	-54.6(5)
N2	C3	C4	N1	-58.2(6)	C1	N1	C4	C3	58.3(6)
N1	C1	C2	N2	56.1(6)	C2	N2	C5	C6	-174.2(4)
C5	N2	C3	C4	176.8(4)	C2	N2	C3	C4	55.4(5)
C5	N2	C2	C1	-177.7(4)	C4	N1	C1	C2	-57.5(6)
C3	N2	C5	C6	64.0(5					

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $(AEP)_2Cu_2Br_6 \cdot 2Br \cdot 2H_2O$

Atom	*x*	*y*	*z*	U(eq)
H2	1536.11	3695.67	7247.63	26
H1E	7335.11	5222.79	9461.29	63
H1F	8102.91	4746.4	8762.4	63
H3A	3801.69	4901.57	7865.62	41
H3B	5364.31	4750.99	8313.96	41
H3C	4127.58	4192.29	8709.76	41
H1A	-474.62	1925.79	5259.67	39
H1B	-1654.23	2768.68	5195.21	39
H5A	3174.1	2434.3	8175.17	34
H5B	3633.73	1912.16	7234.04	34
H3D	2286.41	2461.14	5664.1	33
H3E	2655.34	3739.15	5853.73	33
H1C	-1258.04	3098.97	6806.62	38
H1D	-1611.61	1817.9	6622	38
H2A	938.06	1386.28	6889.13	37
H2B	506.21	2052.69	7777.3	37
H6A	5567.83	3050.04	7774.93	36
H6B	4682.12	3694.38	6901.81	36
H4A	63.81	4171.16	5628.1	38
H4B	489.76	3550.83	4714.15	38

Table S8. Photoluminescent Properties of Different Copper-Based Halides for Comparison

Formula	λ_{ex} (nm)	λ_{em} (nm)	PLQY (%)	FWHM (nm)	Stokes shift (nm)	τ_{ave} (μs)	Ref.
$(C_8H_{14}N_2)CuCl_3·H_2O$	287	532	2.88	105	245	18.91	1
$(C_8H_{14}N_2)CuCl_3$	282	505	3.34	90	223	1.19	
$(C_8H_{14}N_2)CuBr_3$	297	515	35.19	94	218	16.89	
$(C_8H_{14}N_2)CuI_3$	308	522	17.81	106	214	32.93	
$(TMS)_3Cu_2I_5$	340	590	26.88	140	250	4.59	2
$[BAPMA]Cu_2Br_5$	282	526	53.40	101	244	50.2	3
$(R,S\text{-}2\text{-}mpip)_2Cu_2I_6$	300	530	65.96	-	230	7.37	4
$(MA)_4Cu_2Br_6$	302	524	93	107	222	120	5
$(AEP)_2Cu_2I_6·2I·2H_2O$	300	495	97.2	-	145	3.18	6
$[KC_2]_2[Cu_4I_6]$	365	545	97.8	-	180	2.68	7
$PDACuI_3$	300	438	26.5	-	138	0.66	8
$(PPh_4)_2[Cu_2I_4]$	380	545	10	-	165	1.01	9
$(AEP)_2Cu_2Br_6·2Br·2H_2O$	290	510	90.51	96	220	121.1	This work

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