Electronic Supplementary Information

Solvent-induced structrual regulation and luminescence switch of hybrid copper(I) halides for encryption and anti-counterfeiting applications

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Experimental Section:

Materials

Cuprous iodide (CuI, 99%, Aladdin), Ethyltriphenylphosphonium iodide [($EtPh_3P$)I, 95%, Aladdin)], Hypophosphorous acid (H_3PO_2, 50% wt. in H_2O, Aladdin), Methanol (99.5%, GeneralReagent), Ethanol (C_2H_5OH, 99.7%, General-Reagent), Acetonitrile (99.8%, $H_2O \leq 0.001\%$), Acetone (99.7%, Sinopharm). All chemicals were analytically graded and used without further purification.

Syntheses

Synthesis of $(EtPh_3P)_2CuI_3$ (E1). CuI (1 mmol) and ($EtPh_3P$)I (3 mmol) were dissolved in C_2H_5OH (15 mL) and acetonitrile (3 mL). Stirring until the solution is clear and transparent, leaving it at room temperature. Then, as the solvent evaporated, E1 crystals were gradually precipitated and collected.

Synthesis of $(EtPh_3P)_2Cu_2I_4$ (E2). CuI (1 mmol) and ($EtPh_3P$)I (1.5 mmol) were dissolved in C_2H_5OH (15 mL), acetonitrile (3 mL) and H_3PO_2 (0.5 mL). Stirring until the solution is clear and transparent, leaving it at room temperature. Then, as the solvent evaporated, E2 crystals were gradually precipitated and collected.

Synthesis of $(EtPh_3P)Cu_3I_4$ (E3). The synthesis procedure is similar to that of E2, except that the CuI : ($EtPh_3P$)I ratio was changed to 2 : 1.

Preparation of anti-counterfeiting filter membrane. A mixture of 0.5 g E1 powder, 1 g Poly-dimethylsioxane (PDMS) base resin and 0.1 g hardener was printed on filter paper by screen printing method, and then cured at 80 ^{o}C for 12 h.

Characterizations

The single crystal data of E1, E2, and E3 was collected at 293 K using the XtaLAB AFC12 X-ray four-circle single crystal diffractometer (Rigaku) equipped with a CCD-detector using a graphite monochromator and the Cu Kα radiation source. Powder X-ray diffraction (PXRD) patterns were taken on an Aeris PXRD diffractometer (PANalytical Corporation, the Netherlands) operating at 40 kV and 15 mA with a monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). The photoluminescence excitation (PLE), photoluminescence (PL), PL decay spectra and photoluminescence quantum yields (PLQY) measurements were performed on a FLS1000 fluorescence spectrophotometer (Edinburgh Instruments Ltd., UK). The PLQYs were calculated based on the equation: $\eta QE = IS / (ER - ES)$, in which IS denotes the luminescence emission spectral area of the sample, ER is the excitation light spectral area of the null integrating sphere, and ES is the excitation light spectral area of the excited sample. Thermogravimetric analysis (TGA) was conducted on a TG 209F3 from 30 to 500 °C in argon atmosphere with a ramping rate of 10 °C min^{-1}.

Calculation method

Density functional theory (DFT) calculations of three compounds were performed using projector augmented wave (PAW) method based on a generalized gradient approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) format was adopted for the exchange correlation potential for structural relaxation.[1-2] The cutoff energy of a plane-wave basis was set as 520 eV. Monkhorst–Pack mesh of k-point was set as 3 × 1 × 2 for E2. The atoms in each compound were fully relaxed until the Hellmann–Feynman forces on them were within 0.01 eV Å^{-1}. The electronic iteration convergence was set as 10^{-5} eV. To consider the strong Coulomb repulsion for the Cu-3*d* electrons, we use a Hubbard correction to PBE (GGA+U).[3]

Figure Captions:

Table S1. The crystal structure parameters of $(EtPh_3P)_2CuI_3$, $(EtPh_3P)_2Cu_2I_4$, and $(EtPh_3P)Cu_3I_4$.

Table S2. The calculated total energy of $(EtPh_3P)_2CuI_3$, $(EtPh_3P)_2Cu_2I_4$, $(EtPh_3P)Cu_3I_4$ and $EtPh_3PI$.

Table S3. Bond Valence Sum (BVS) calculations for Cu atom in E1, E2 and E3.

Figure S1. The simulated and experiment PXRD patterns of E1.

Figure S2. The simulated and experiment PXRD patterns of E2.

Figure S3. The simulated and experiment PXRD patterns of E3.

Figure S4. The asymmetric unit of (a) E1, (b) E2 and (c) E3.

Figure S5. Tauc phot of E1.

Figure S6. Tauc phot of E2.

Figure S7. Tauc phot of E3.

Figure S8. The photo images of the sample socking in the water for different days under 365 nm UV light.

Figure S9. The PL spectra of E1 socking in the water for 27 days.

Figure S10. The PL spectra of E2 socking in the water for 27 days.

Figure S11. TGA curves of E1, E2, and E3.

Figure S12. XPS pattern of E1.

Figure S13. XPS pattern of E2.

Figure S14. XPS pattern of E3.

Figure S15. Photographs of E1 under 365 nm UV light excitation before and after adding ethanol, methanol, water, glycol, isopropanol and glycerol.

Table S1. The crystal structure parameters of $(EtPh_3P)_2CuI_3$, $(EtPh_3P)_2Cu_2I_4$, and $(EtPh_3P)Cu_3I_4$.

Compound	$(EtPh_3P)_2CuI_3$ (E1)	$(EtPh_3P)_2Cu_2I_4$ (E2)	$(EtPh_3P)Cu_3I_4$ (E3)
Formula	$C_{40}H_{40}CuI_3P_2$	$C_{40}H_{40}Cu_2I_4P_2$	$C_{20}H_{20}Cu_3I_4P$
Molecular weight	1026.90	588.51	989.55
Temperature (K)	150	150	150
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4
a (Å)	9.0870 (6)	8.6790 (2)	12.7409 (3)
b (Å)	13.1972 (4)	20.4707 (4)	25.0723 (5)
c (Å)	17.3600 (6)	11.8536 (2)	7.9544 (2)
α (°)	90	90	90
β (°)	116.1350 (10)	96.136(2)	106.194 (2)
γ (°)	90	90	90
V (Å^3)	3925.8 (2)	2093.91 (7)	2440.16 (10)
ρ_{calc} (g/cm^3)	1.737	1.867	2.694
μ (mm^{-1})	3.024	4.065	7.723
Reflections measured	91796	29150	34132
Reflections independent	8031	6324	7355
R_{int}	0.0709	0.0486	0.0617
R_1 [$I > 2$sigma(I)]^a	0.0285	0.0335	0.0326
$wR(F^2)\cdot$[$I > 2$sigma(I)]^b	0.0500	0.0404	0.0383
Goof	1.015	1.037	1.051
$\Delta\rho_{max}, \Delta\rho_{min}$ (e.Å^{-3})	0.427, -0.349	1.094, -0.979	1.471, -1.780

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2. The calculated total energy of $(EtPh_3P)_2CuI_3$, $(EtPh_3P)_2Cu_2I_4$, $(EtPh_3P)Cu_3I_4$ and $EtPh_3PI$

Compound	$(EtPh_3P)_2CuI_3$	$(EtPh_3P)_2Cu_2I_4$	$(EtPh_3P)Cu_3I_4$	$EtPh_3PI$
Total Energy (eV)	-526.2918	-531.0776	-549.0856	-521.7326

Note: The possible transformation pathway:

$$2(EtPh_3P)_2CuI_3 = (EtPh_3P)_2Cu_2I_4 + 2(EtPh_3P)I \qquad (1)$$

$$E_t = -531.0776 - 2*521.7326 - 2*(-526.2918) = -521.9592 \text{ eV} < 0$$

$$3(EtPh_3P)_2Cu_2I_4 = 2(EtPh_3P)Cu_3I_4 + 4(EtPh_3P)I \qquad (2)$$

$$E_t = -2*549.0856 - 4*521.7326 - 3*(-531.0776) = -1591.8688 \text{ eV} < 0$$

The transformation energy is defined as energy difference of final production and initial materials.

Table S3. Bond Valence Sum (BVS) calculations for Cu atom in E1, E2 and E3.

E1		E2		E3	
Atom	BVS	Atom	BVS	Atom	BVS
Cu1	0.89	Cu1	0.9	Cu1	0.84
				Cu2	0.85
				Cu3	0.91

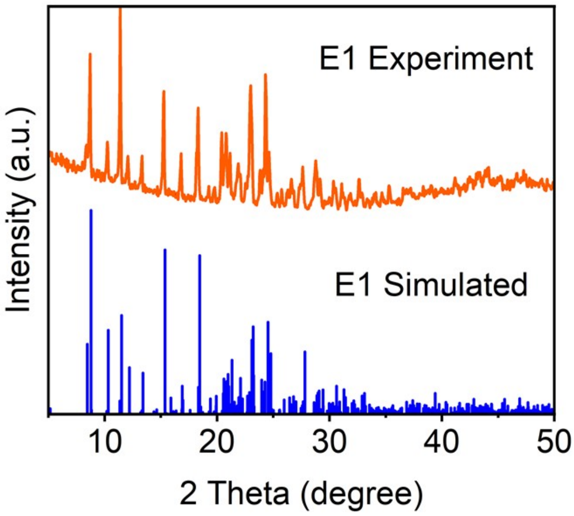

Figure S1. The simulated and experiment PXRD patterns of E1.

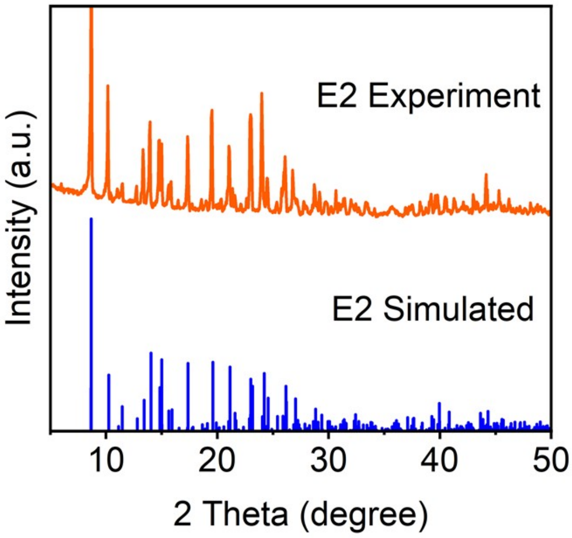

Figure S2. The simulated and experiment PXRD patterns of E2.

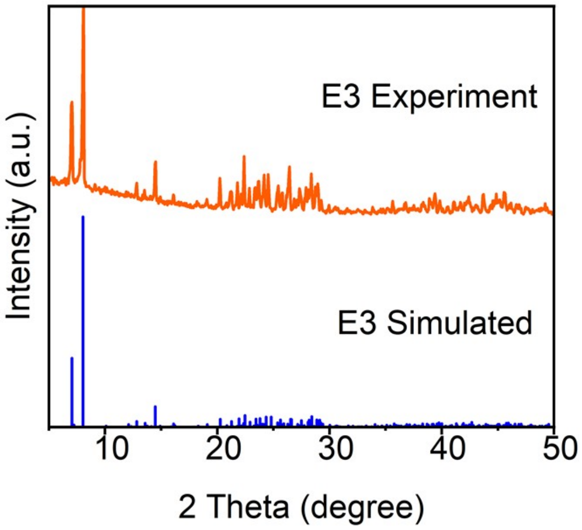

Figure S3. The simulated and experiment PXRD patterns of E3.

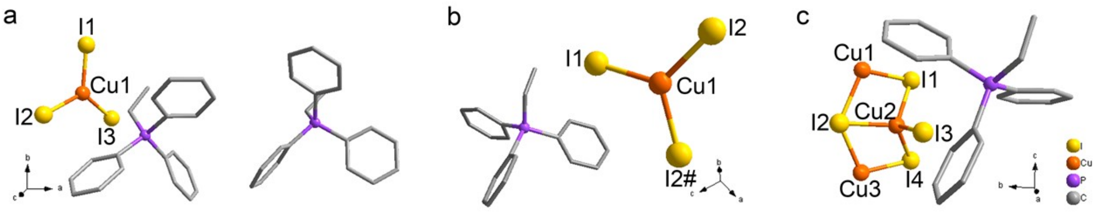

Figure S4. The asymmetric units of (a) E1, (b) E2 and (c) E3.

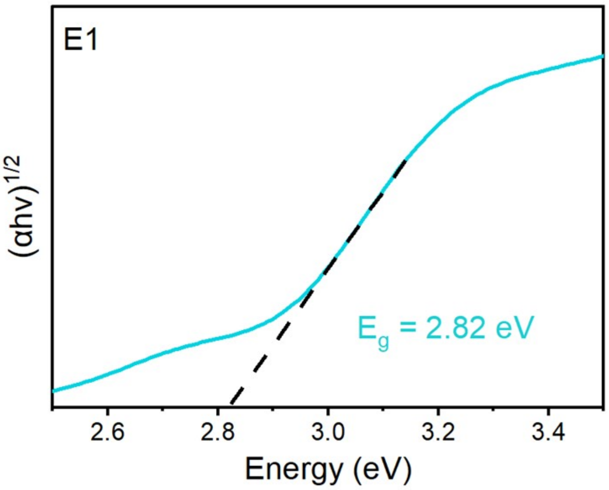

Figure S5. Tauc phot of E1.

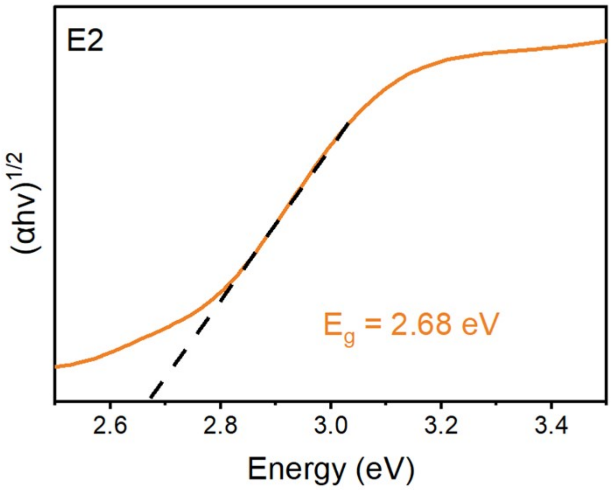

Figure S6. Tauc phot of E2.

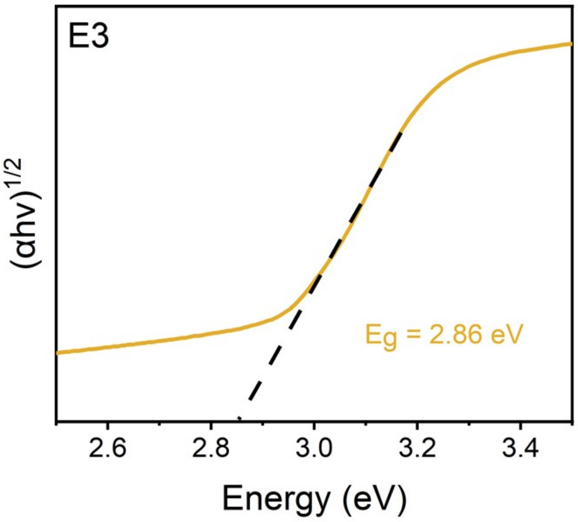

Figure S7. Tauc phot of E3.

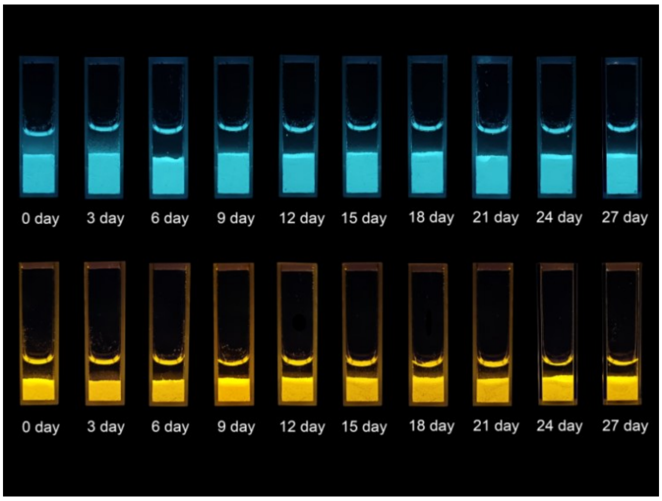

Figure S8. The photo images of the sample socking in the water for different days under 365 nm UV light.

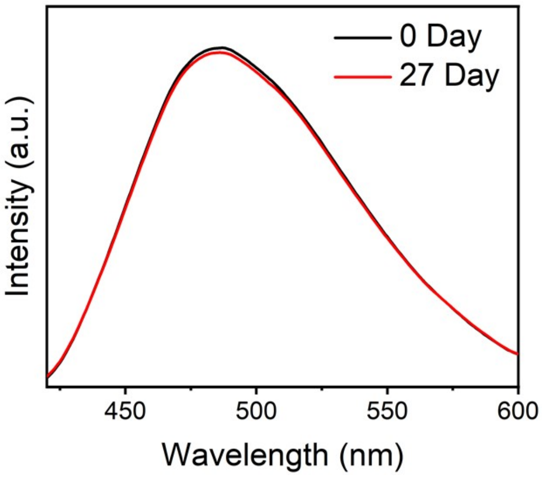

Figure S9. The PL spectra of E1 socking in the water for 27 days.

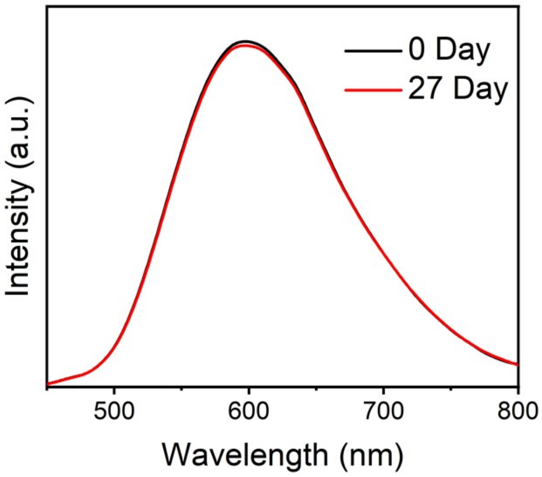

Figure S10. The PL spectra of E2 socking in the water for 27 days.

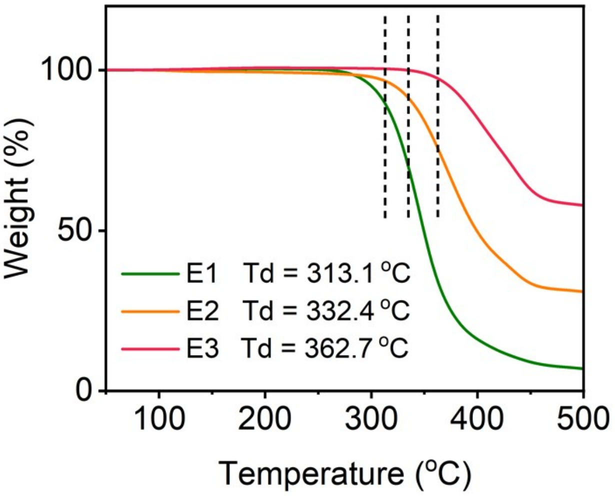

Figure S11. TGA curves of E1, E2, and E3.

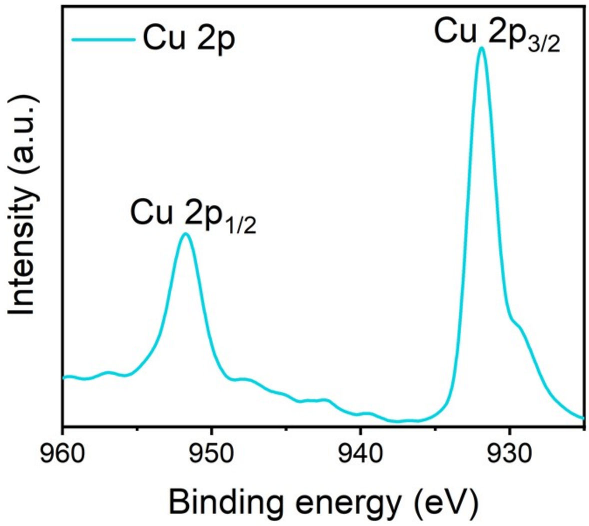

Figure S12. XPS pattern of E1.

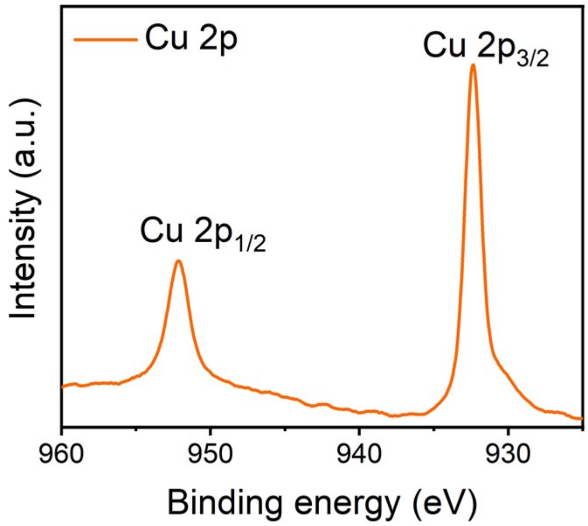

Figure S13. XPS pattern of E2.

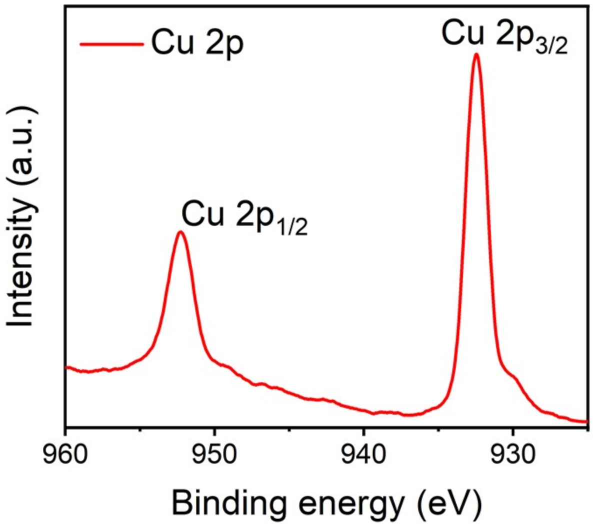

Figure S14. XPS pattern of E3.

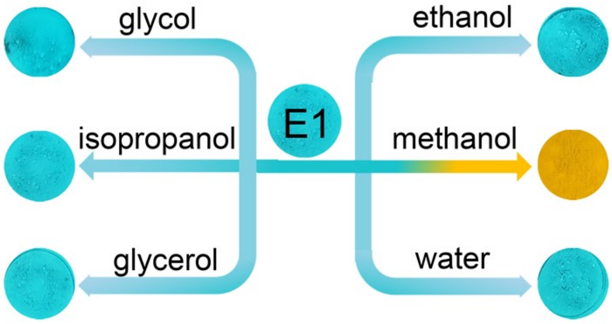

Figure S15. Photographs of E1 under 365 nm UV light excitation before and after adding ethanol, methanol, water, glycol, isopropanol and glycerol.

References

1 J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1977, **78**, 1396.

2 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.

3 V. I. Anisimov, J. Zaanen and O. K. Andersen, *Phys. Rev. B.,* 1991, **44** (3), 943-954.