Electronic Supplementary Material (ESI) for CrystEngComm.

Support information

Chemical Etching Strategy to Preparation Microtubes of Hybrid Organic Cuprous Halide

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Experiment

Materials

Triphenylphosphine (MACKLIN 99%), Potassium bromide (GENERAL-REAGENT 99%), Ethanol (GENERAL-REAGENT 99.7%), Methylamine hydrobromine (Aladdin 98%), Copper substrate (2 cm×5 cm×0.1 cm, Jianwei Co.Ltd), Graphite electrode (Inner Mongolia Wanxing carbon co.ltd), N,N-Dimethylformamide (MACKLIN 99.5%). Fluorescent dyes (Jinan Lixia blue feather new decorative materials shop), non-fluorescent dyes (Chengdu Painter Art Materials Co., Ltd).

Characterization

Single crystal X-ray diffraction data were collected using Supernova CCD diffractometer with graphite-monochromated Mo Kα radiation (λ =0.71073 Å) at room temperature. Experimental PXRD patterns were measured by Bruker D8 ADVANCE diffractometer with Cu Kα radiation (λ = 1.54178 Å). PL spectra and PLQY were measured on Edinburgh FS5 fluorescence spectrometer with 2 nm slit width. Solid-state UV–visible absorption spectra (UV–vis) were recorded on Shimadzu 2600 UV–vis spectrometer at room temperature in the range from 800 nm to 240 nm. $BaSO_4$ is utilized as a standard that possesses 100% reflectance. FTIR was recorded on Nicolet iS10 using KBr pellet technique within the range from 4000 to 400 cm^{-1}. MAISHENG MP6010D provides the direct voltage required for electrochemical synthesis. The digital photos under ambient and 365 nm light were collected by OLYMPUS BX53M. The 3D morphology was measured by OLYMPUS DSX1000. Scanning electron microscope (SEM) was recorded on ZEISS Gemini 300. Thermogravimetric analysis (TGA) were recorded on NETZSCH STA 449F3 with a heating rate of 10 K min^{-1} under N_2 atmosphere.

Computational Details

The partial density of state (PDOS) of BTC were calculated by using the CASTEP software. For this calculation, the Perdew-Burke-Ernzerhof-General-Gradient-Approximation (PBE-GGA) of the exchange correlation functional was used. Energy cutoff was 351eV, k-point set as 1×1×1, and the Brillouin zone path set as G-F-Q-Z-G. The molecular orbitals of BTC were calculated using the DMol3 module in Material Studio software. The Brillouin zone was sampled by using gamma points. The other parameters were set as default.

Preparing of BTC

0.0262 g (0.1 mmol) of triphenylphosphine was dissolved in 20 mL ethanol and marked as A. 0.0119 g (0.1 mmol) potassium bromide was dissolved in 100μL water and marked as B. The mixture of A and B was stirred for half hour. The cathode of the potentiostat was connected to the copper sheet, while the anode was connected to the graphite electrode. Copper substrate and graphite electrode are soaked in precursor solution completely. The direct voltage was set as 0.6 V. After 24 h reaction, the colorless crystal attached to copper sheet was collected for further characterization.

Preparing of CTC

CTC was synthesized with similar procedures of BTC using potassium chloride instead of potassium bromide.

Preparing of BTC microtubes

5 mg of BTC powder and 0.5 mg of methamide hydrobromine were dissolved in 1 mL N,N-dimethylformamide with 20 minutes ultrasonic dispersion. The solution was placed still in a fume hood. By slowly evaporation, the colorless BTC microtube was obtained after several days.

Preparing of photonic multicolor microtubes

The solution of fluorescent and non-fluorescent dyes was filled into microtube by capillarity.

The red fluorescent (Y_2O_3:Eu@water-based acrylic resin) and the blue fluorescent ($BaMgAl_{10}O_{17}$:Eu@water-based acrylic resin) were purchased from Jinan Lixia blue feather new decorative materials store. The non-fluorescent dyes were purchased from Chengdu Painter Art Materials Co., Ltd

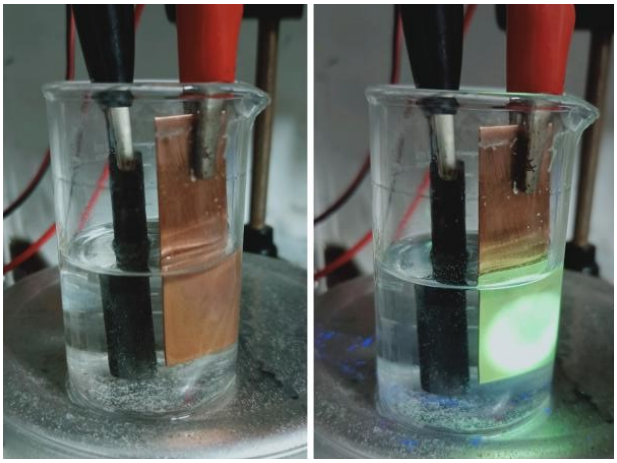


Figure S1. The device of electrochemical synthesis under ambient light (left) and 365 nm light (right).

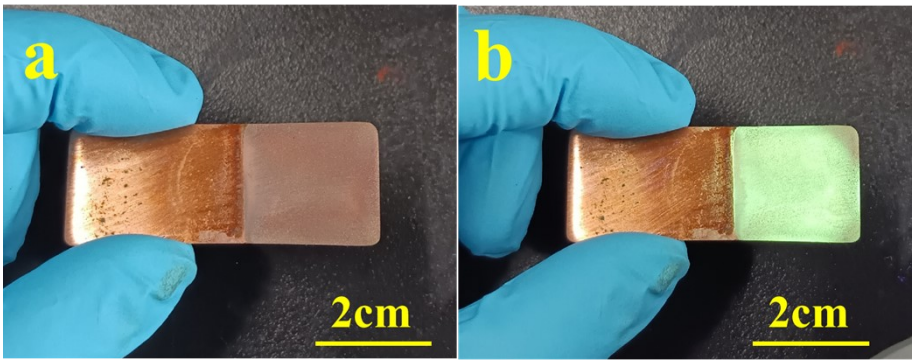


Figure S2. Digital photos of copper substrates after electrochemical synthesis under ambient light (a) and 365 nm light (b).

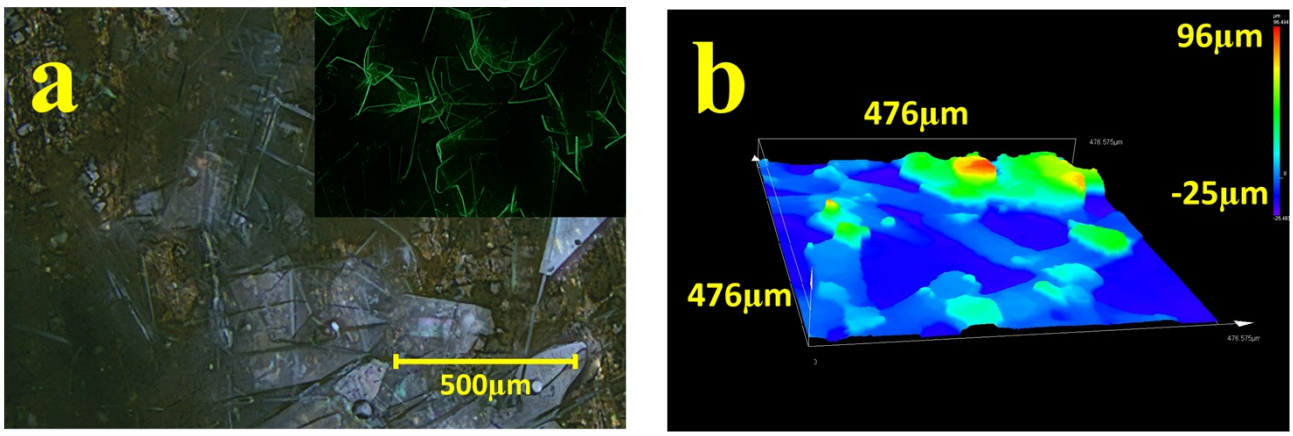


Figure S3. Digital images (a) and 3D colorful morphology (b) of BTC on the copper substrate after electrochemical synthesis for 12 h.

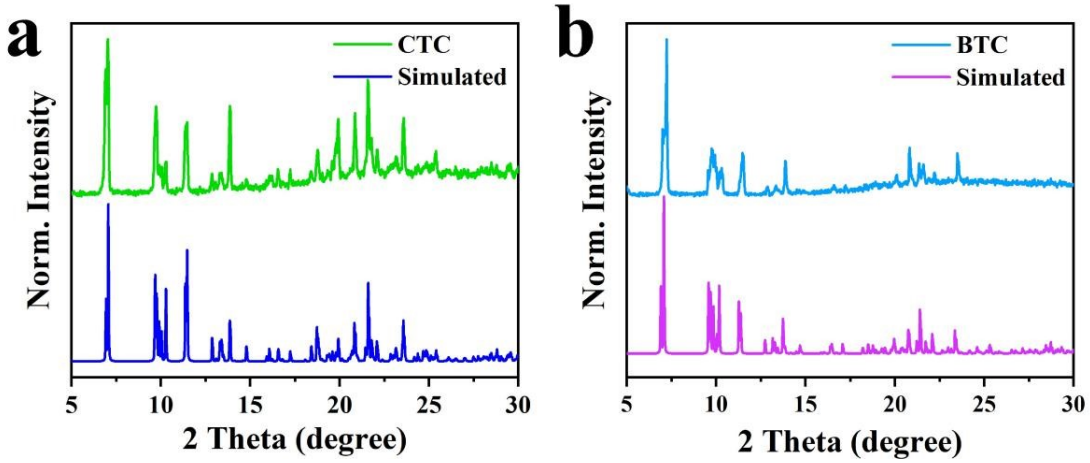


Figure S4. PXRD of CTC (a) and BTC (b).

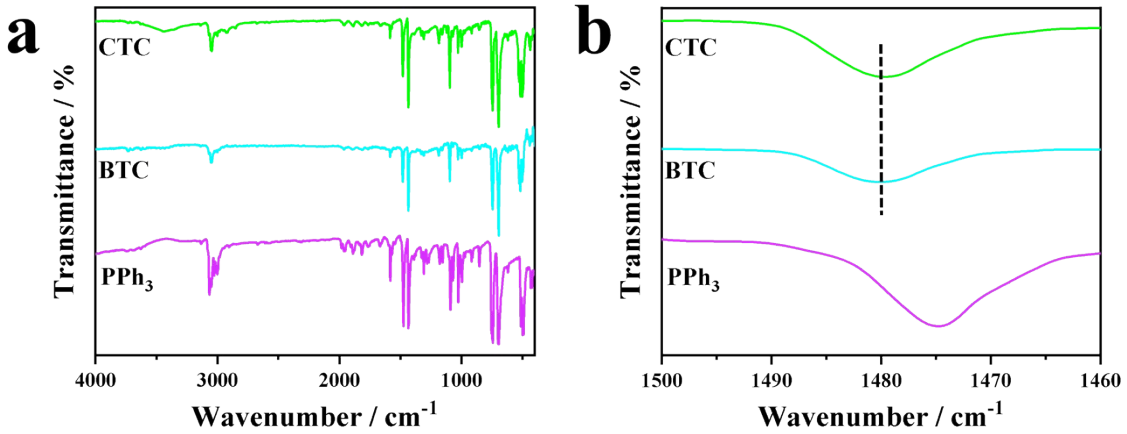


Figure S5. The FT-IR spectra (a) and topical FT-IR spectra (b) of the CTC (green), BTC (cyan) and PPh_3 (purple).

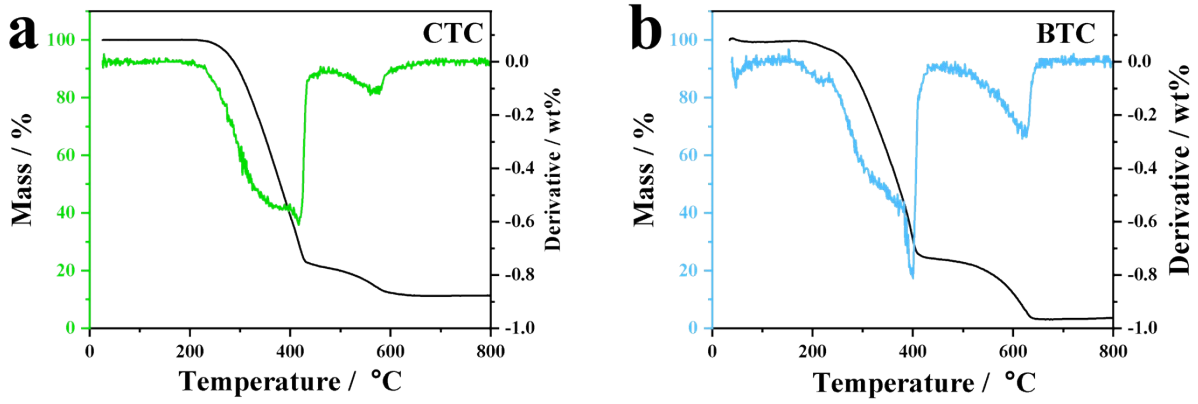
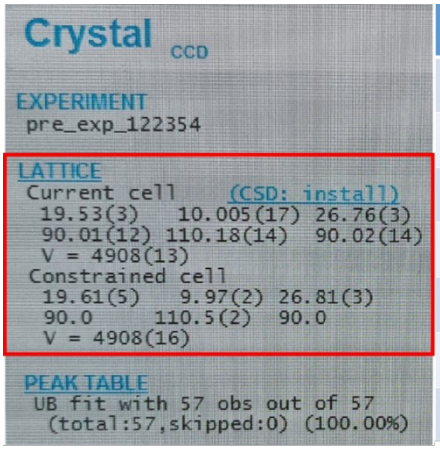


Figure S6. TGA curves of CTC (a) and BTC (b).



	Microtubes	cif 755912	cif 1131990
a	19.53(3)	19.435(5)	19.27
b	10.005(17)	9.933(3)	9.81
c	26.76(3)	26.580(7)	27.02
α	90.01(12)	90.000	90.00
β	110.5(2)	110.067(4)	112.08
γ	90.02(14)	90.000	90.00
V	4908(13)	4819.71	4733.22

Figure S7. Experimental unit cell of BTC crystalline microtube. Single-crystal X-ray diffraction analysis reveals that the as-synthesized BTC microtube is the same with the one of compound with CCDC number 755912. The single crystal information of CTC listed as CCDC number 1131990.

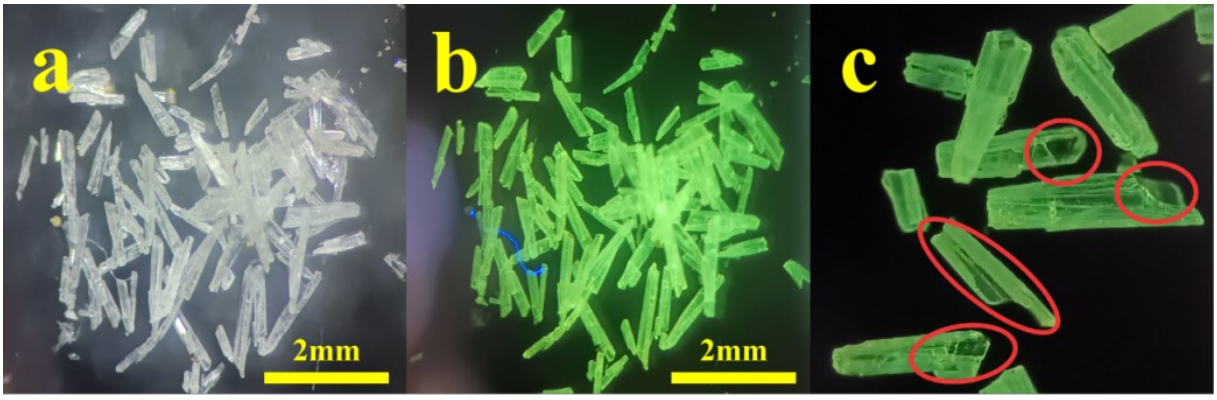


Figure S8. The digital photos of microtubes under ambient light(a) and 365 nm(b), and the channels of BTC microtubes marked by red circle.

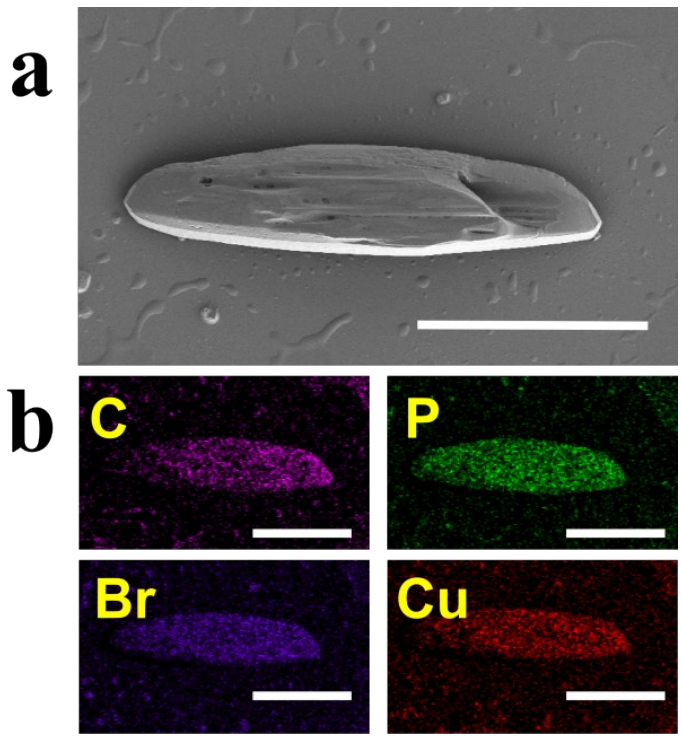


Figure S9. SEM (a) and EDS elemental mapping (b) of BTC microtube (scale bars are 250 μm).

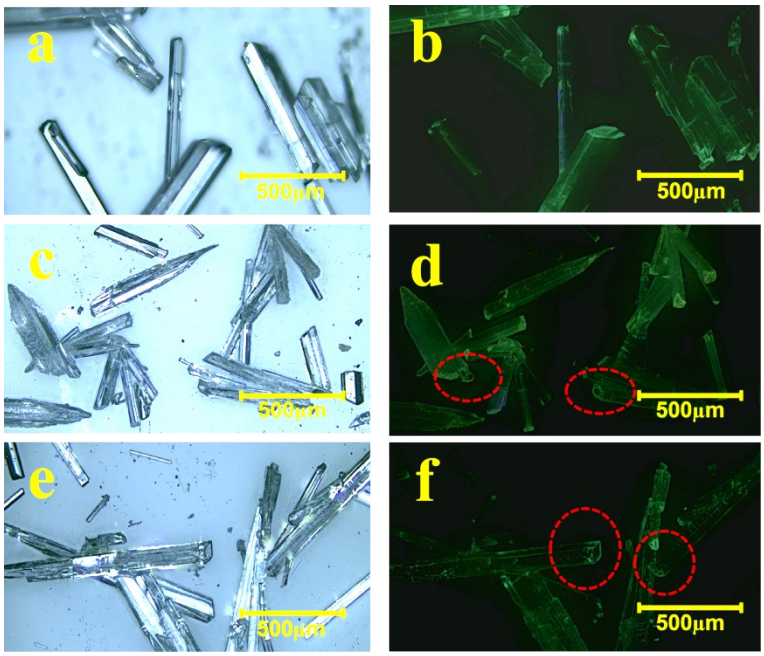


Figure S10. Digital photos of BTC crystals with different etchant:BTC mass ratio 0:5 (a, b), 0.25 : 5 (c, d), and 0.5 : 5 (e, f) under ambient light and 365 nm. The channels of microtubes are marked by red circles.

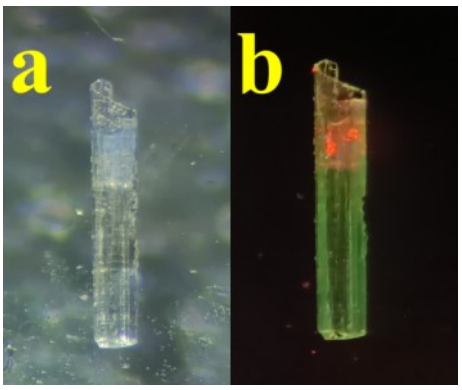


Figure S11. Photos of partly filled BTC microtube with red fluorescent dye under ambient light (a) and 365nm irradiation (b).

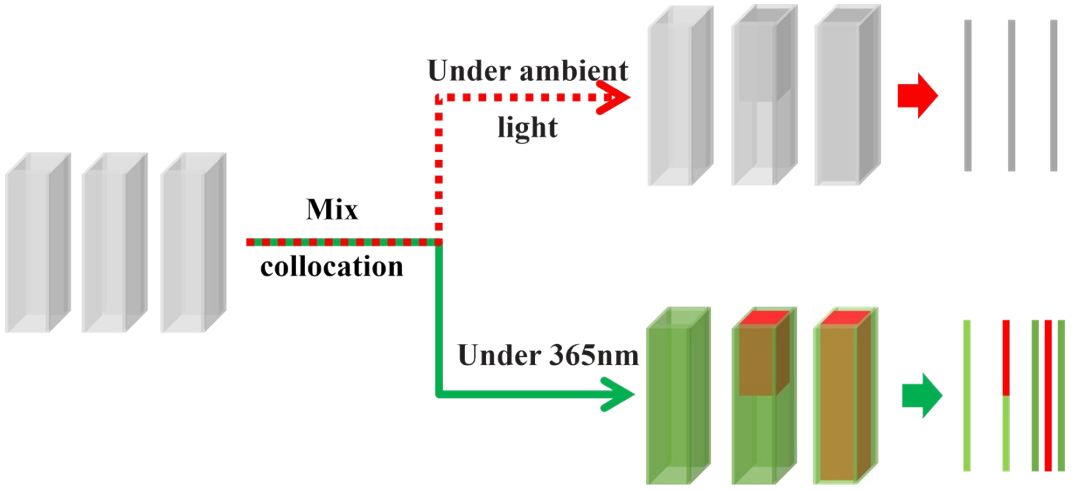


Figure S12. Schematic illustration of the encoding strategy based on the photonic multicolor barcodes.