Electronic Supplementary Material (ESI) for Materials Advances.

Copper(I) Iodide Organic-inorganic Hybrid Luminescent Inks for Anti-counterfeiting Application

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Supporting Information

Experimental Section

Materials. 2-(diphenylphosphino)ethyltriethoxysilane ($PPh_2(CH_2)_2Si(OCH_2CH_3)_3$, *dpes*, 97 %, Macklin); Copper(I) iodide (CuI, 99.5%, Aladdin); Tetraethyl orthosilicate (TEOS, 98%, Macklin); Triethoxyvinylsilane (VTES, 97%, Macklin); Methyltriethoxysilane （MTES, 98%, Macklin); Phenyltriethoxysilane (PTES, Macklin); Dichloromethane (AR, Macklin), N,N-dimethylformamide (>99.9 %, Macklin); All reagents and solvents were used as received without further purification unless otherwise stated.

Synthesis of c-TEOS, c-VTES, c-MTES, c-PTES. At room temperature, 2-(diphenylphosphino)ethyltriethoxysilane (1 g, 2.66 mmol) was added to the suspension of CuI (0.5 g, 2.62 mmol) in dichloromethane (10 mL). After stirring the mixture at room temperature for 2 h, the mixture was filtered. After the solvent evaporated, Cu_4I_4-*dpes*, the colorless oily substance with high viscosity, was obtained. Yield is 77 % based on Cu. Then, the mixture was mixed with Cu_4I_4-*dpes*: TEOS molar ratio of 2×10^{-3}:1, dissolved in solvent DMF, added with a small amount of hydrochloric acid of pH 2.5, and stirred for 5 h. After the solvent evaporated, a colorless and transparent viscous liquid was formed, and the sol of **c-TEOS** was obtained. Similarly, by replacing TEOS with VTES, MTES, PTES in the same proportion, sols of **c-VTES**, **c-MTES** and **c-PTES** (Figure S1) were respectively obtained.

Preparation of the coatings on quartz glass sheets. The four sols synthesized in the previous step were spin-coated (3000 r/min, 30 s) on quartz glass sheets, and then cured at 60 °C for 2 hours to obtained uniform coatings that emits yellow light under 254 nm UV irradiation.

Preparation of the powdery samples. After the coatings on the quartz glass sheets were fully cured, scraped off the coatings and grind them with an agate mortar to get the white powder sample.

Powder X-ray diffraction (PXRD). PXRD analyses were carried out on a Rigaku Ultima IV automated diffraction system using Cu Kα radiation (λ=1.5406 Å). The data were collected at room temperature in a 2θ range of 5-60° with a scan speed of 10°/min. The operating power was 40 kV/40 mA.

Fourier transform infrared spectroscopy (FT-IR). FT-IR measurements were performed on a Nicolet 6700 Contiuμm spectrometer (Thermo Scientific). The coating samples were pressed onto a KBr pellet and placed into the sample chamber of the infrared spectrometer. All spectra were recorded in transmission mode with a frequency range of 450-4000 cm^{-1}.

Optical diffuse reflectance measurements. Optical diffuse reflectance spectra were measured at room temperature on a Shimadzu UV-3600 spectrophotometer. Data were collected in the wavelength range of 250-800 nm. $BaSO_4$ powder was used as a standard (100% reflectance).

Thermogravimetric (TG) analysis. TG analyses of the coatings were performed on a STA449F3 (NETZSCH). Pure powder samples were loaded into platinum pans and heated with a ramp rate of 10 K/min from 30 °C to 810 °C.

Photoluminescent (PL) measurements. Photoluminescence (PL) measurements of coatings on quartz were carried out on an Edinburghinstruments, FS5 spectrophotometer at room temperature. Room temperature PL lifetime decay curves were collected on LifeSpec II (Edinburgh Instruments).

Internal quantum yield (IQY) measurements. IQY values were measured on a C9920-02 quantum yield measurement system (Hamamatsu Photonics) with 150 W xenon monochromatic light source and 3.3 inch integrating sphere at room temperature. Samples for internal quantum yield measurements were prepared by spreading fine powder samples evenly on the bottom of a quartz sample holder.

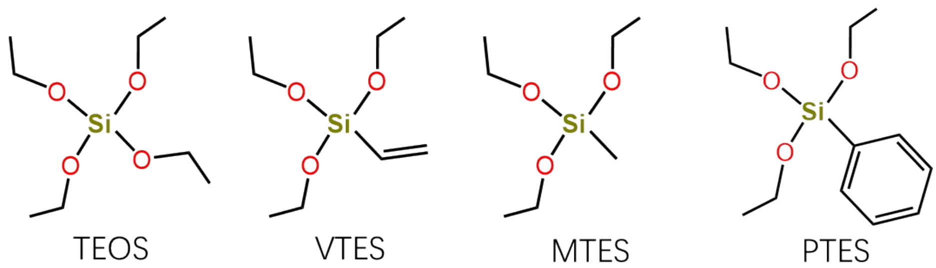

Figure S1. The chemical structures of the coupling reagents.

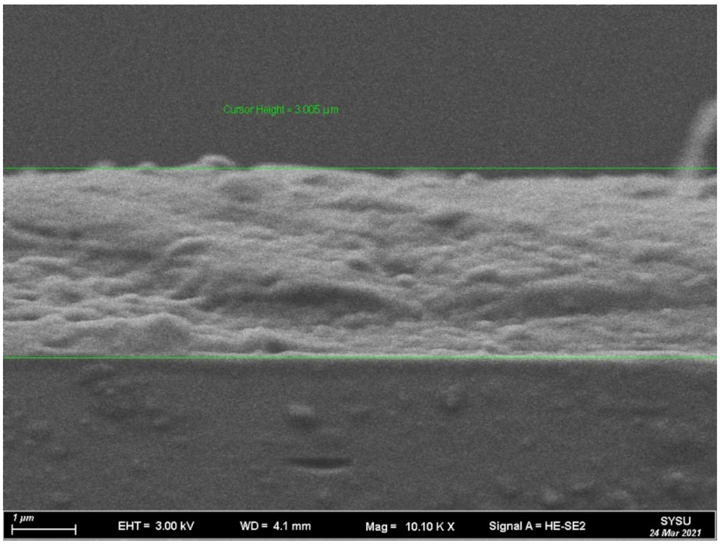

Figure S2. SEM image of the cross section of glass-based c-PTES by spin coating (3000 r/min, 30 s).

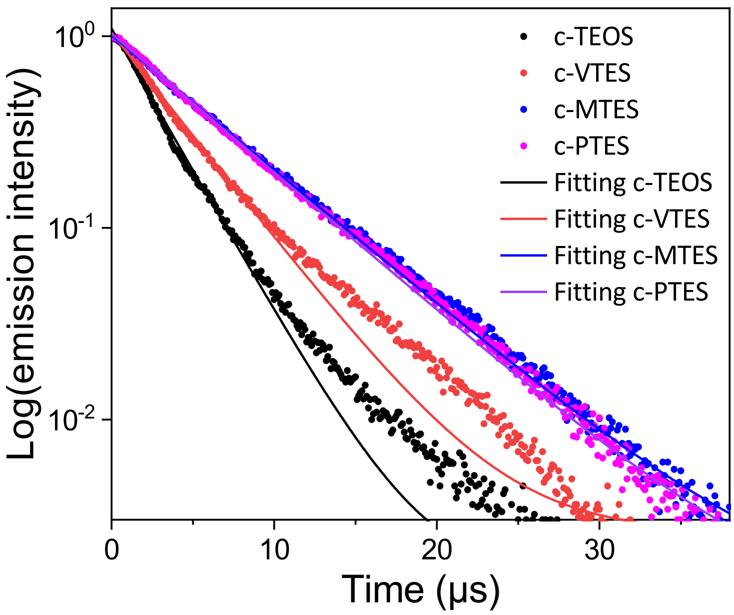

Figure S3. Luminescent decay plots and fitting curves of **c-TEOS**, **c-VTES**, **c-MTES**, and **c-PTES**.

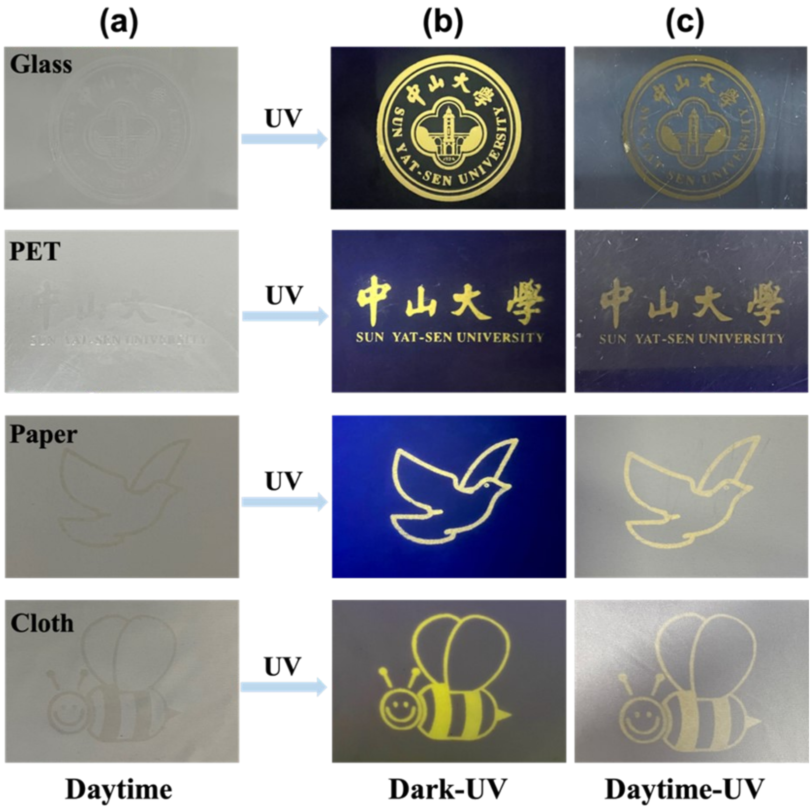

Figure S4. Photos of fluorescent patterns printed on different base materials (commercial glass, PET, paper and cloth) under natural light (a), 254 nm UV light in the dark (b) and 254 nm UV light in the daytime (c).

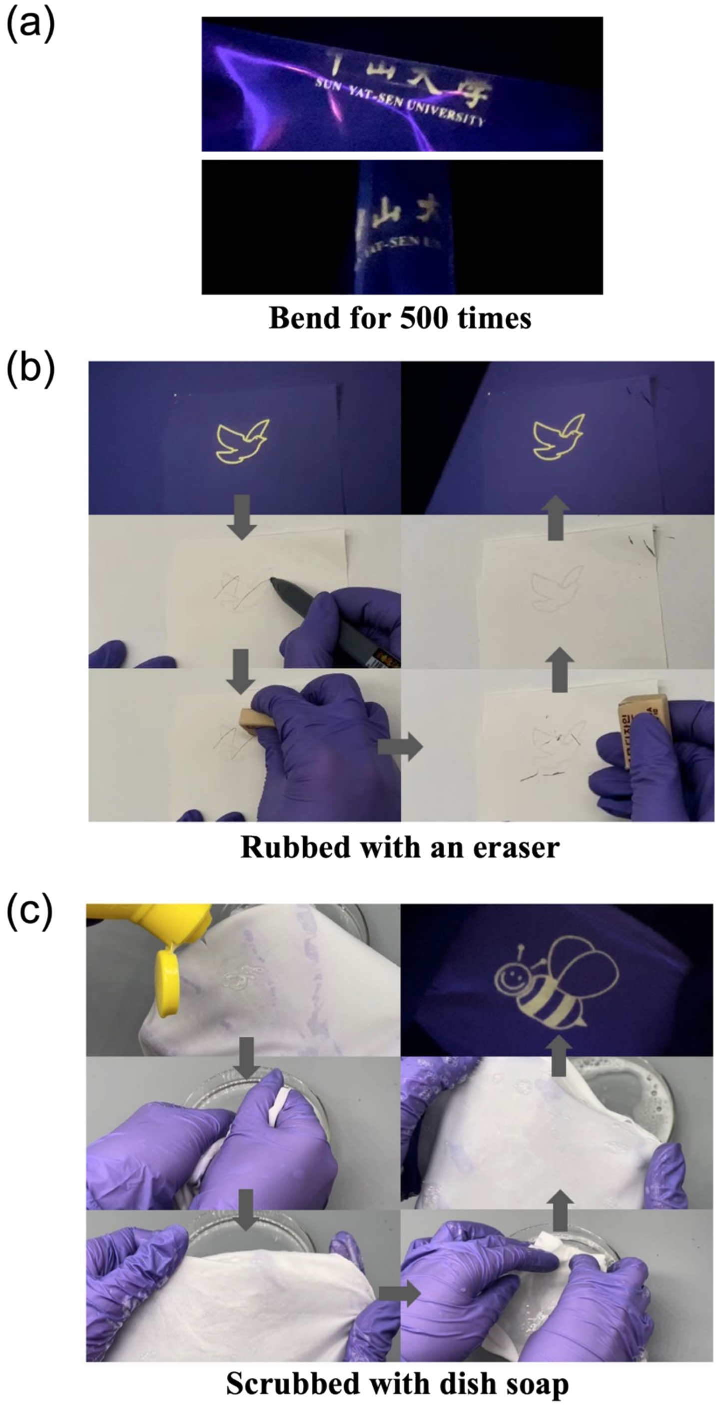

Figure S5. (a) The photo after bending the PET film with the logo of Sun Yat-sen University horizontally and vertically for 500 times. (b) The pigeon pattern printed on the paper was rubbed with eraser for 100 times. (c) The small bee pattern printed on the textile was scrubbed with detergent and water for 10 times.