Electronic Supporting Information (ESI)

Starch based Near-Infrared Organic Fluorophores for Imaging of Latent Fingerprints

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1. Materials and methods

1.1 Materials

All reagents for organic synthesis were commercially available and used as received without further purification. Commercial fingerprint red phosphor were purchased from Beijing BoNa HengDa Technology. 405 nm LED lamp (3W) was purchased from ANJOET. Porous starch is purchased from store "Biological raw materials extracted from plants", and the production batch number is BCKZSW210413-2.

1.2 Methods

1.2.1 Characterization Methods

The compound was confirmed by High resolution mass spectroscopy (GCT-MS Micromass, UK) and 1H-NMR (400 MHz, 293K). The absorption spectra were recorded by Shimidazu UV-3600 UV-VIS-NIR spectrophotometer and the fluorescence spectra were measured by a FluoroMax-4 (Horiba). The fluorescence lifetimes and quantum yields were measured based on Edinburgh Instrument FLS1000 Integrating sphere.

1.2.2 Preparation of single crystals

We dissolved 10 mg of the compound in 1ml dichloromethane, then added 0.5 ml ethanol to it, stood still, and obtained a single crystal after the solution evaporated slowly.

1.2.3 Collection of fingerprints

The volunteers were asked to lightly touch their foreheads with their fingers and then pressed their fingers on the different substrate surfaces.

1.2.4 Development of LFPs by powder dusting method.

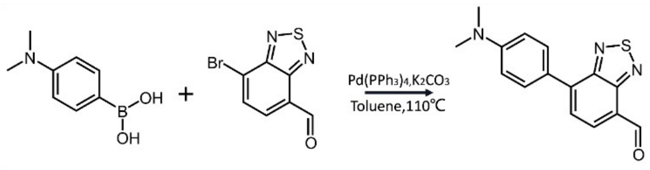
We put 3 mg of BrBTN and 20 mg of porous starch in a mortar for grinding until the mixture is visible to the naked eye. A small amount of fingerprint powders were carefully added on these substrates printed with LFPs for about 10 s. Then excessive powders could be gently blown away by rubber suction bulb.

1.2.5 Image acquisition equipment.

The LFP images were obtained under 405 nm LED lamp (ANJOET-501B, 3W). Grayscale analysis was performed by ImageJ software from the National Institutes of Health (U.S.).

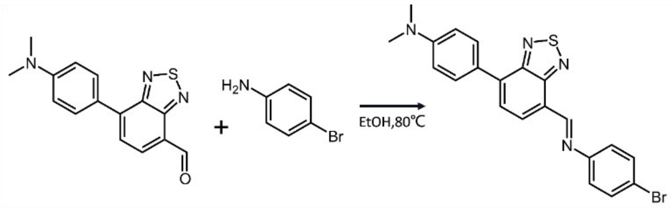
2. General procedure for the synthesis of target compounds

Scheme S1 Synthesis route of DBT.



7-bromobenzo[1,2,5]thiadiazole-4-carbaldehyde(1.45g,6mmol), 4-(dimethylamino) phenylboronic acid (1g, 6.2mmol) and $Pd(PPh_3)_4$ (0.25g, 0.22 mmol) were dissolved in toluene (50 mL) and stirred under argon. K_2CO_3 solution (2M, 1.5 mL) was added via syringe. The reaction was heated to 110 °C and refluxed for 24 h. The obtained crude product was concentrated under reduced pressure and subjected to column chromatography (CH_2Cl_2/hexanes 1：1) to yield the product as a red solid (1.17g, 69%).

Scheme S2 Synthesis route of BrBTN.



DBT (282mg，1mmol) and 4-bromoaniline (204mg，1.2mmol) were taken into the branch reactor, 5ml ethanol was added, argon was filled, heated and refluxed for 5-8h, cooled, washed with ethanol or recrystallized and purified to obtain dark red powder(322mg，74%).

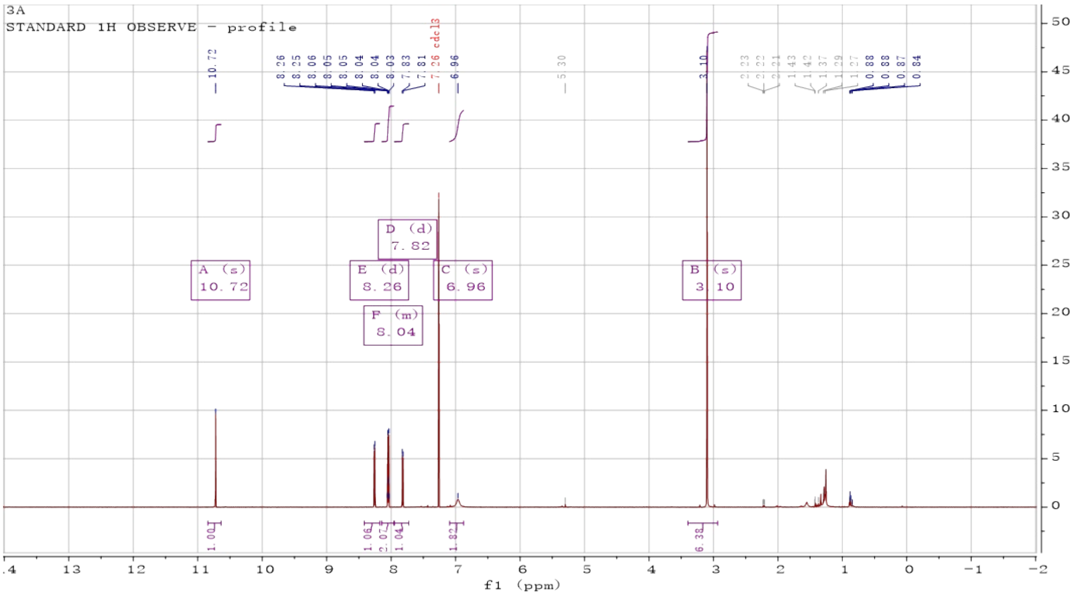


Fig.S1 ^{1}HNMR spectrum of compound DBT

^{1}HNMR (600 MHz, Chloroform-d) δ 10.72 (s, 1H), 8.26 (d, J = 7.5 Hz, 1H), 8.14 – 7.96 (m, 2H), 7.82 (d, J = 7.4 Hz, 1H), 6.96 (s, 2H), 3.10 (s, 6H)

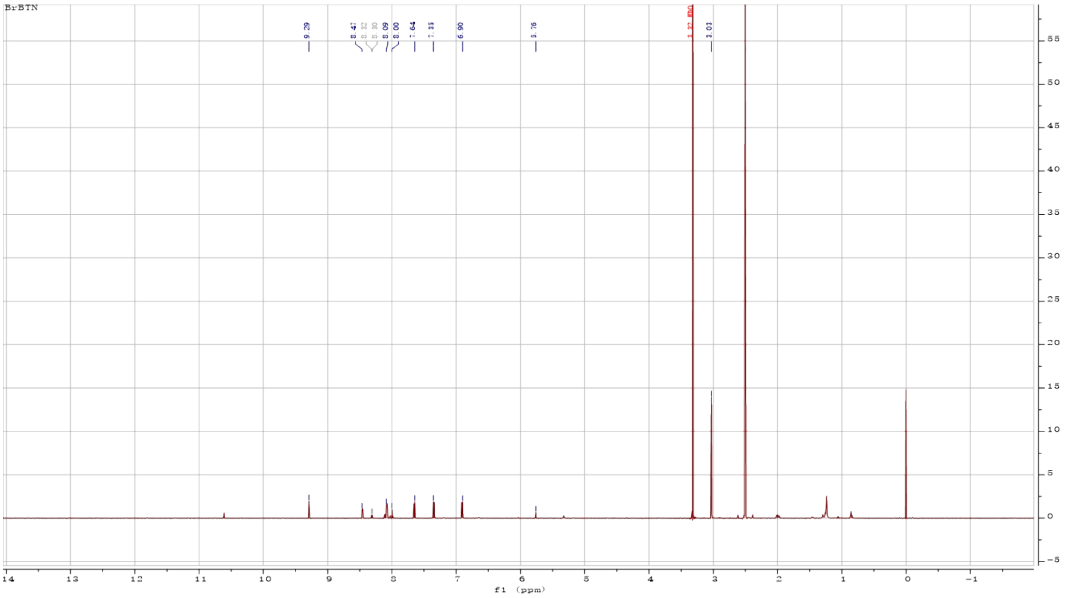


Fig.S2 ^{1}HNMR spectrum of compound BrBTN

^{1}HNMR (600 MHz, DMSO-d6) δ 9.29 (s, 1H), 8.47 (s, 2H), 8.09 (s, 2H), 8.00 (s, 2H), 7.64 (s, 1H), 7.35 (s, 2H), 6.90 (s, 2H), 3.03 (s, 6H).

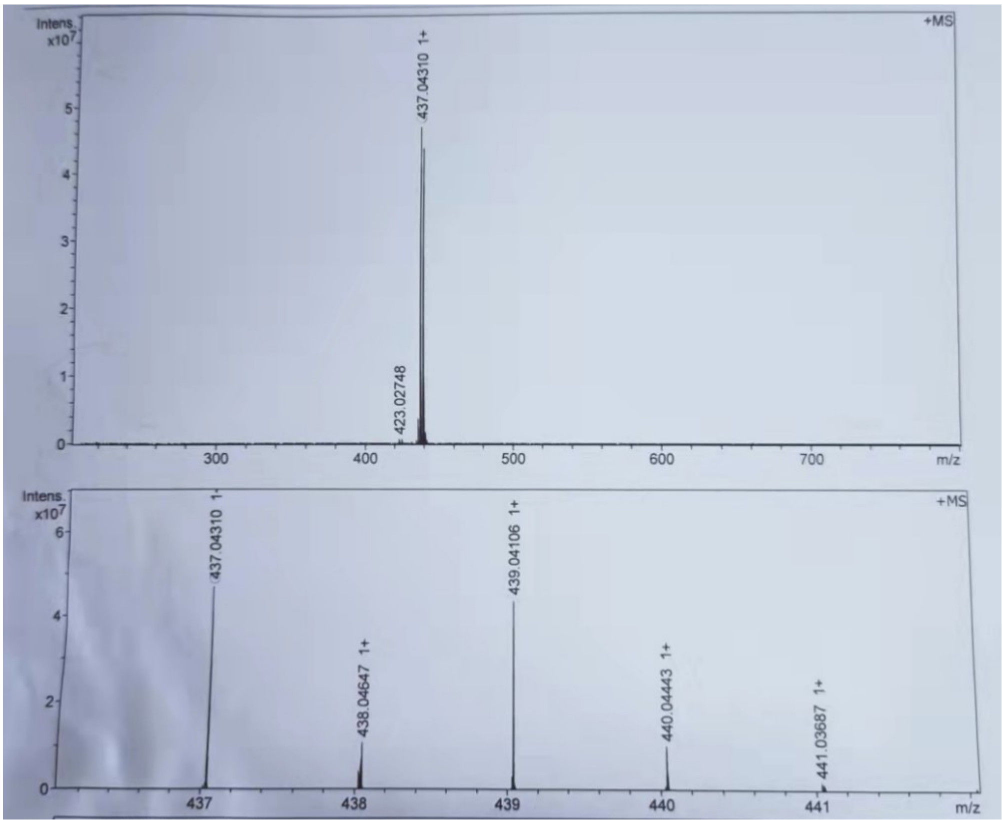


Fig.S3 HR-MS (MALDI-MS) spectrum of BrBTN

HR-MS (MALDI-MS) spectrum of IM-1, m/z = 437.

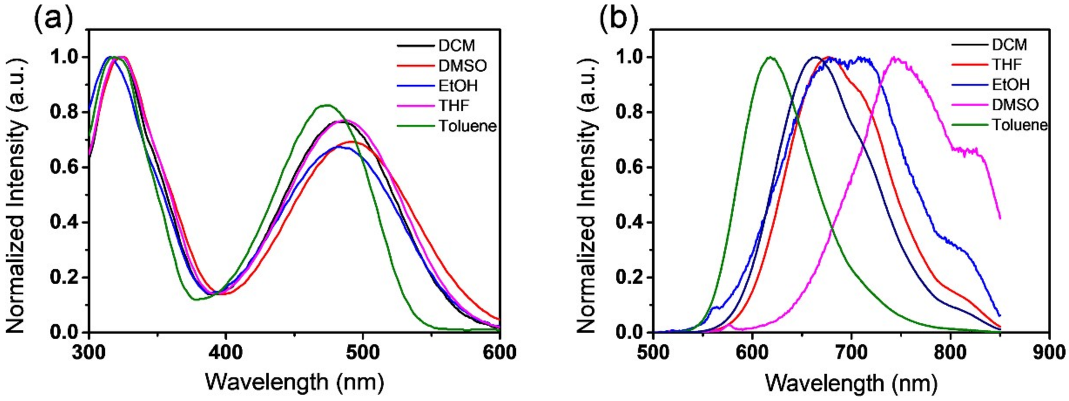


Fig. S4 The UV absorption spectra (a) and FL emission spectra of BBTN (b), measured in the different solvents with different polarity.

Table S1. Detailed photo-physical data of BrBTN in the different solvents.

	solvent	ε (20℃)	Δf	a L*mol-1*cm-1	λ_{abs} (nm)	λ_{em} (nm)	Stokes' Shift(nm)	Φ	τ (ns)	k_r (ns^{-1})	k_{nr} (ns^{-1})
	Powder					675		0.209	2.03	0.103	0.389
BrBTN	Toluene	2.37	0.014		475	618	143	0.489	1.02	0.479	0.500
	DCM	9.10	0.218	30534	479	667	188	0.388	1.26	0.308	0.486
	THF	7.58	0.210	39243	485	677	192	0.198	1.58	0.125	0.508
	EtOH	24.3	0.288		478	707	229	0.067	1.66	0.040	0.562
	DMSO	48.9	0.264		493	728	235	0.016			

(ε: dielectric constant; Δf: solvent oriented polarizability; a: molar extinction coefficient; Φ: quantum yield; τ:life time; k_r: radiation transition rate; k_{nr}: non-radiation transition rate)

- The absorption maxima of BrBTN molecules varied slightly between 475 and 493 nm in different solvents (Fig. S4a).
- The fluorescence emission shows a high sensitivity to the solvent polarity. The emission maximum (λ_{em}) was gradually red-shifted with increasing the solvent polarity from a dielectric constant (ε) of toluene ($\varepsilon = 2.37$, $\lambda = 618$ nm), DCM ($\varepsilon = 9.10$, $\lambda_{em} = 667$ nm) to DMSO ($\varepsilon = 48.9$, $\lambda_{em} = 728$ nm).
- Moreover, as shown in Table S1, BrBTN had large Stokes' shift between the absorption and emission maxima and the Φ of BrBTN molecules is greatly reduced in high polarity solvents such as ethanol as well as DMSO.
- The radiative decay rates (k_r) and the nonradiative decay rates (k_{nr}) were calculated based on equations of $k_r = \Phi / \tau$ and $\Phi = k_r / (k_r + k_{nr})$. BrBTN presented a single-exponential PL decay process, yielding a decreased radiative-rates from 0.479 to 0.040 ns^{-1} and almost same nonradiative decay rates of 0.486-0.562 ns^{-1}, respectively.

- These were all the typical characteristics of CT state luminescence.

Table S2. Summary of the single crystals data of BrBTN.

Identification code	BrBTN
Empirical formula	$C_{21}H_{17}BrN_4S$
Formula weight	437.36
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.0016(5)
b/Å	7.9310(4)
c/Å	14.9592(10)
α/°	90
β/°	100.488(6)
γ/°	90
Volume/Å^3	933.46(10)
Z	2
ρ_{calc}g/cm^3	1.556
μ/mm^{-1}	4.148
F(000)	444.0
Crystal size/mm^3	0.14 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.008 to 146.902
Index ranges	$-6 \le h \le 9$, $-9 \le k \le 8$, $-17 \le l \le 17$
Reflections collected	3440
Independent reflections	2788 [R_{int} = 0.0359, R_{sigma} = 0.0524]
Data/restraints/parameters	2788/1/247
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1215
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.1262
Largest diff. peak/hole / e Å^{-3}	0.43/-0.70
Flack parameter	-0.12(4)

- According to the single-crystal data, the average volume occupied by a single dye molecule in the crystal lattice is 0.47 nm^3
- According to the Eigenvalue algorithm method[1], the molecular size is about 0.38 nm^3.

The average volume occupied by a single dye molecule in the crystal lattice is much larger than its molecular size.

Table S3 Bond Lengths for BrBTN

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C4	1.890(5)	C5	C6	1.393(9)
S1	N2	1.610(6)	C7	C8	1.458(8)
S1	N3	1.612(5)	C8	C9	1.372(9)
N1	C1	1.419(7)	C8	C13	1.432(9)
N1	C7	1.276(9)	C9	C10	1.416(7)
N2	C13	1.355(8)	C10	C11	1.381(9)
N3	C12	1.357(8)	C11	C12	1.419(8)
N4	C17	1.364(8)	C11	C14	1.479(8)
N4	C20	1.438(8)	C12	C13	1.450(8)
N4	C21	1.454(8)	C14	C15	1.416(8)
C1	C2	1.385(9)	C14	C19	1.411(9)
C1	C6	1.396(10)	C15	C16	1.383(8)
C2	C3	1.411(9)	C16	C17	1.410(8)
C3	C4	1.361(9)	C17	C18	1.422(9)
C4	C5	1.387(10)	C18	C19	1.369(9)

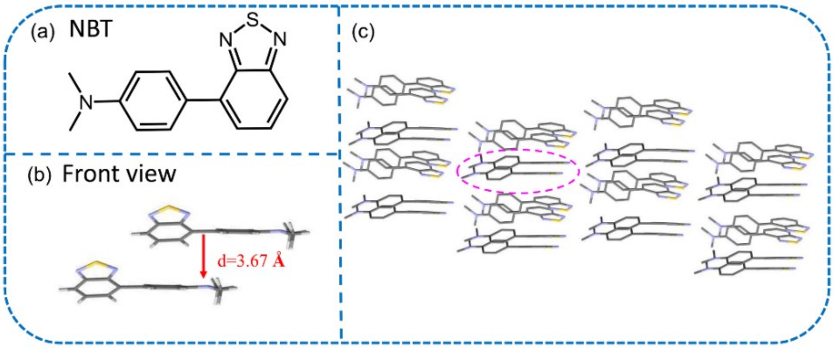


Fig.S5 (a) The molecule structure of 4-(benzo[c][1,2,5]thiadiazol-4-yl-)N,N-dimethylaniline(NBT). Front view (b) of local packing modes of two adjacent molecules. (c) Packing modes of molecules view down the π-stacking axis of single crystals of NBT.

- The single crystal data of 4-(benzo[c] [1,2,5] thiadiazol-4-yl)-N, N-dimethylaniline (NBT) was obatained from Cambridge Crystallographic Data Centre (CCDC number:1421224). The crystal structures with NBT display the average distance between adjacent molecules of 3.67 Å according to the reported result. [2]

  According to the single-crystal data of the BrBTN, the centroid-to-centroid distance between two adjacent molecules in π-stack is as large as 3.80 Å.
- As a result, the block group “bromophenyl with imine” might rotate freely around the benzothiadiazol unit and effectively inhibit π-π stacking among the molecules,

thus avoid the quenching of fluorescence in either the solid state or aggregate state.

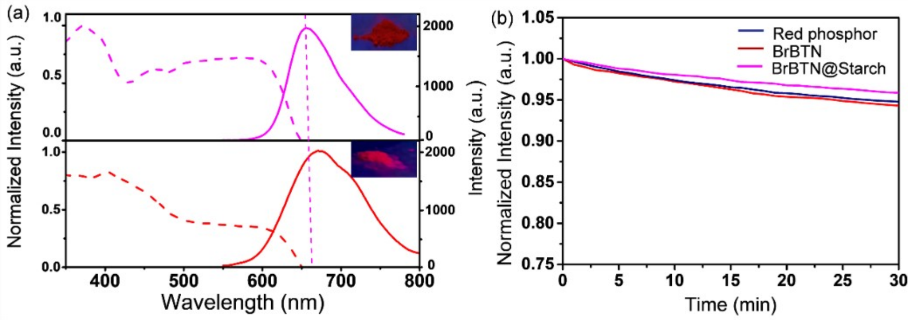


Fig.S6 (a) Excitation and emission spectra of BrBTN@Starch (top) and BrBTN. (bottom) powders. (b) The photo-bleaching kinetic traces of BrBTN@Starch (pink line), BrBTN powders (red line) and commercial red phosphor powders (blue line) on glass substrate under 405 nm.

- The excitation and emission spectra of BrBTN@Starch placed on a glass substrate were measured. The excitation spectrum exhibited a strongly maximum around 380 nm, with additional bands around 590 nm, also exhibiting good light absorption ability in the visible spectrum range. The maximum emission peak of BrBTN is 665 nm, which exhibited a blue shift of 10 nm compared with BrBTN solid powder. The blue-shift might originate from the intermolecular interaction between starch and BrBTN.
- The photostability of the prepared BrBTN@Starch was further studied under continuous excitation (405 nm), using a light source built in fluorometer with a power of 2.0 mW as determined by a laser power meter. The intensity of BrBTN@Starch dropped by less than 5% after 30 min irradiation at 405 nm (pink line in Figure S6b), exhibiting better good photostability than BrBTN powders (red line in Figure S6b) and commercial red phosphor powders (blue line in Figure S6b).

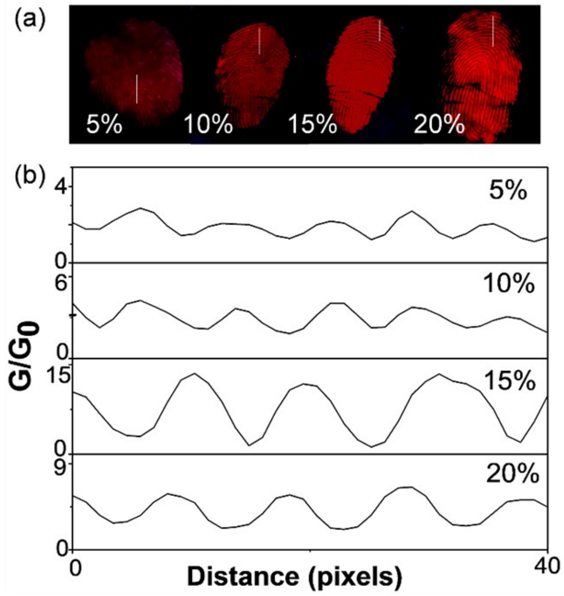


Fig.S7 The composite image and gray ratio image of 0.5mg, 1mg, 1.5mg, 2mg

BrBTN doped with porous starch. Fingerprints of (a) are all from volunteer 3.

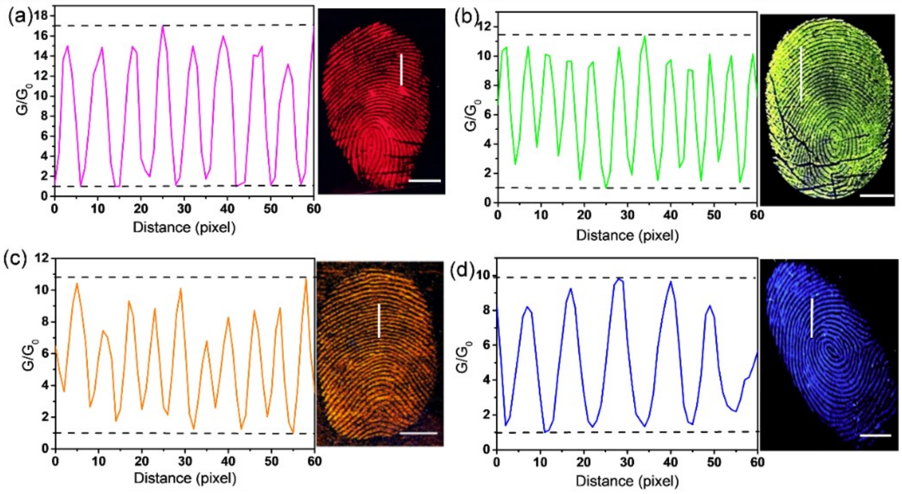


Fig.S8 Gray ratio image(left) and image(right) of LFPs on quartz glass sheet of BrBTN@Starch powders (a), PMs-N_2H_4 powders [3] (b), Boc PZ DCM/MMT powders [4] (c) and fluorescent starch powder [5](d). The scale bar is 5 mm.

- We have obtained the gray ratios of the potential fingerprint images of new materials on glass provided by the other reported literatures. Their grayscale value (G) was extracted by using Image J software. The gray scale ratio of the image based on PMs-N_2H_4 shown in Figure S9b is less than 12. The image gray scale ratio of Boc PZ DCM/MMT shown in Figure S9c is less than 11. The image gray scale ratio of fluorescent starch powder is less than 10.
- Compared to the reported nanoparticles, the LPF images based our material exhibited a higher resolution with a high gray scale ratio of 17, which benefited from its NIR emission with high brightness and the high selectivelty.

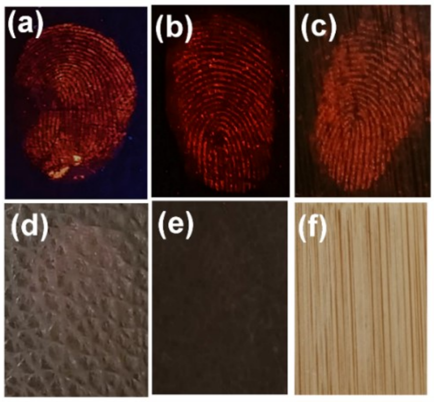


Fig.S9 (a)-(c) Imaging photo on leatherwear (a), cardboard (b), wood (c) under 405 nm irradiation. (d)-(f) are the corresponding images under sunlight. Fingerprints of (a) is from volunteer 3. Fingerprints of (b) and (c) are from volunteer 2.

- The fluorescence images of LFP on leatherwear, cardboard and wood substrates were collected under 405 nm irradiation with a realme X7 Pro mobile phone as the signal collector. LFP with high resolution were obtained on these substrates.

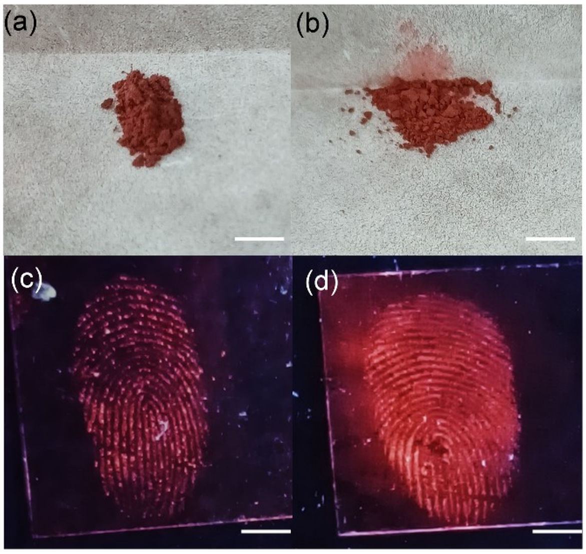


Fig.S10 BrBTN@Carbon nanotubes (25%) (a) and BrBTN@ SiO_2(20%) (b) powders under sunlight. The scale bar is 2cm. Image of LFP on quartz glass sheet of BrBTN@Carbon nanotubes (25%) (c) and BrBTN@SiO_2(20%) (d) under 405 nm lamp. The scale bar is 5mm.

- The porous nanoparticles of silica, carbon nanotubes and other related reagents were purchased from the company Innochem.
- And the BrBTN powder were mixed with silica (20%) and carbon nanotubes (25%) to form new composite materials, respectively.
- Based on these powders，the clear fingerprint images both with strong red fluorescence were obtained.

3.References

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