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Supporting Information

Covalent Organic Polymers for Rapid Fluorescence Imaging of Latent Fingerprints

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S1. Experimental Section

S1.1 Chemicals and Materials

1,3,6,8-tetrabromopyrene (TBP), 1,4-Dibromonaphthalene (DN), 2,2'-Dipyridyl, bis(1,5-cyclooctadiene)nickel ($Ni(cod)_2$), N,N-Dimethylformamide (DMF) and 1,5-cyclooctadiene (cod) were purchased from J&K Scientific Ltd. Lysozyme, palmitic acid, squalene and glucose were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Chloroform ($CHCl_3$), tetrahydrofuran (THF) and ethanol were purchased from Beijing Chemical Works. Unless otherwise specified, all reagents were used directly without further processing. Glass slides were Feizhou Glass Co. Ltd, which size is 25.4 mm × 75.6 mm and its thickness is 1 ± 0.2 mm. Glass spotted capillary were purchased from Huaxi Medical University Instrument Factory, which inner diameter is 0.3 mm and the tube length is 100 mm.

S1.2 Synthesis of Materials

The COP materials (COP-101 ~ COP-105) were synthesized by nickel-catalyzed Yamamoto-type Ullmann cross-coupling reaction, which use 1,3,6,8-tetrabromopyrene (TBP) as one monomer and 1,4-Dibromonaphthalene (DN) as another monomer in different ratios. The synthetic route of the COPs was shown in Scheme 1, and the specific experimental process were as follows. First, cod (0.505 mL, 3.96 mmol, dried with CaH_2), $Ni(cod)_2$ (1.125 g, 4.09 mmol), and 2,2'–bipyridyl (0.640 g, 4.09 mmol) were added to dry DMF (65 mL) in the pressure flask, and the mixture was stirred at 40 °C until completely dissolved, and purple solutions were obtained in this process. Then, the monomer DN and TBP with different ratio were

added to the pressure flask containing purple solutions, the specific amount of the monomer added was listed in Table S1. Next, the pressure flask with above reagents was kept stirring at 80 °C for 12 h. All above experiments were carried out in a glove box under an argon atmosphere. After the reaction completed, the mixture cooled down to the room temperature. Subsequently concentrated HCl was added to the above purple suspension, and this operation would turn the solution from purple into light green transparent. After filtration, the residue was washed by $CHCl_3$ (5×15 mL), THF (5×15 mL) and H_2O (5×15 mL), respectively. Then the solid residues were dried in a vacuum oven of 140 °C for 24 h. The dried sample (named as COP-101, COP-102, COP-103, COP-104 and COP-105) was placed in containers after grinding and stored in a desiccator. The specific synthetic experimental processes and reaction conditions of the five COPs are keep the same except the amounts of the two monomers added (Table S2).

S1.3 Characterization of Materials

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 8700 instrument with the wave number range of 4000 - 400 cm^{-1}. Thermal gravimetric analysis (TGA) data were obtained on a STA449C (NETZSCH) instrument with a heating rate of 10 °C / min under flowing N_2 atmosphere. Scanning electron microscope (SEM) images were obtained on a JSM-6701F SEM instrument. N_2 adsorption/desorption isotherms at 77 K were measured by a Micrometrics ASAP 2020. Pore size distributions were calculated by the N_2 sorption isotherms based on the nonlocal density functional theory (NLDFT) model in the Micrometrics ASAP

2020 software package. The fluorescence images of latent fingerprint were carried out by Olympus IX73 microscope, where λex = 550 nm. The fluorescent spectra of solid state powder monomers and the COP materials were measured by Hitachi F-7000 Fluorescence Spectrophotometer with a PMT voltage of 330 V and a scan speed of 240 nm / min, and the width of the excitation slit is 5 nm and emission slit is 5 nm for the COPs.

S1.4 Collection and Detection of LFPs

All LFP samples were collected from six volunteers, and a variety of different substrates (glass slides, ironware, plastic bags, paper, aluminum foil, etc.) were used for fingerprint collection and imaging. The volunteers were asked to rub their fingers on their foreheads and then pressed their fingers on the chosen substrate surfaces. Meanwhile, the COP materials powder were evenly sprayed on the surface of the fingerprint so that the COP materials could completely covers the whole fingerprint, and subsequently used the washing ear ball is used to blow away the sprayed extra COP powders. Finally, putted fingerprints under an ultraviolet (UV) lamp (λex=365nm), and collected pictures by using a Nikon D5200 digital camera. During detecting aged fingerprints experiments, we put the fingerprints that pressed on the glass slides in a proper fresh box and stored 45 days at room temperature. The operation of the aged fingerprints imaging process is in consistent with the previous operation of fresh fingerprints. In addition, we simulated the rainy environment through the experiment by soaking the LFPs deposited on the glass slide in a water environment and shaking for a few minutes, then take out the glass slide to dry

naturally and the LFPs imaging process is the same as aforementioned. All the above experiments are carried out at room temperature, and the other experimental conditions are also consistent.

S2. Supplementary Tables and Figures

Table S1 The amount of monomer DN and TBP of the COP materials, and the fluorescent data of the solid COP materials.

Material	ratio of DN:TBP	DN/mmol	TBP/mmol	λex/nm	λem/nm	Intensity (a.u.)
DN				342	509	373
TBP				412	440	626
COP-101	1:0	0.942	0	397	479	4626
COP-102	16:1	0.8393	0.0523	354	492	2971
COP-103	8:1	0.7536	0.0942	340	523	1607
COP-104	2:1	0.471	0.2355	468	544	1059
COP-105	0:1	0	0.471	487	603	709

Table S2 The porosity property of the COP materials.

Material	BET SSAs [m^2/g]	Pore volume [cm^3/g]	Pore size [nm]
COP-101	55.457	0.2	4.47, 11.11, 14.88, 25.21
COP-102	70.396	0.23	3.99, 6.86, 25.06
COP-103	210.87	0.251	0.778, 2.38, 5.5, 7.4, 12.6
COP-104	474.67	0.283	0.685, 2.14, 2.67, 3.37
COP-105	1231.88	0.719	0.611, 2.44, 3.33

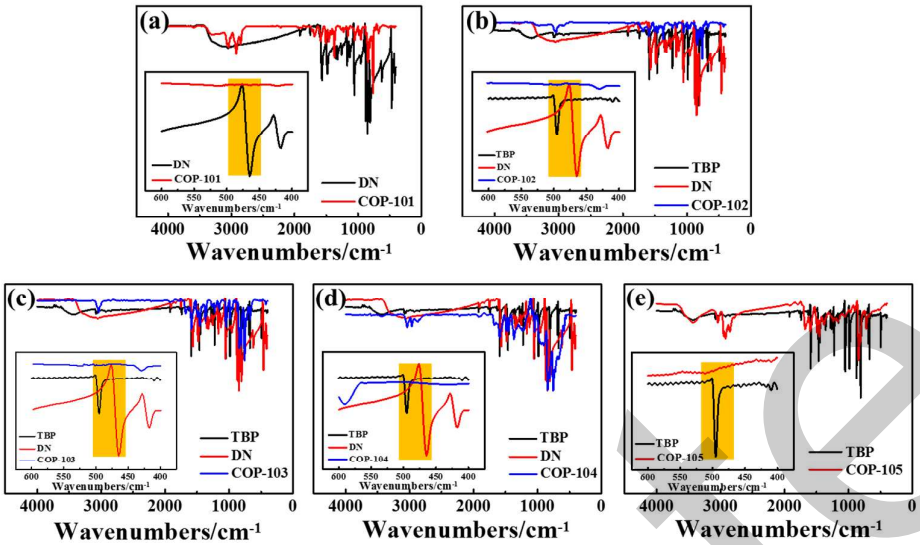

Figure S1 FTIR spectra of the COP materials and the corresponding monomers from 400-4000 cm^{-1} and 400-800 cm^{-1} (the inset). **(a)** COP-101; **(b)** COP-102; **(c)** COP-103; **(d)** COP-104; **(e)** COP-105.

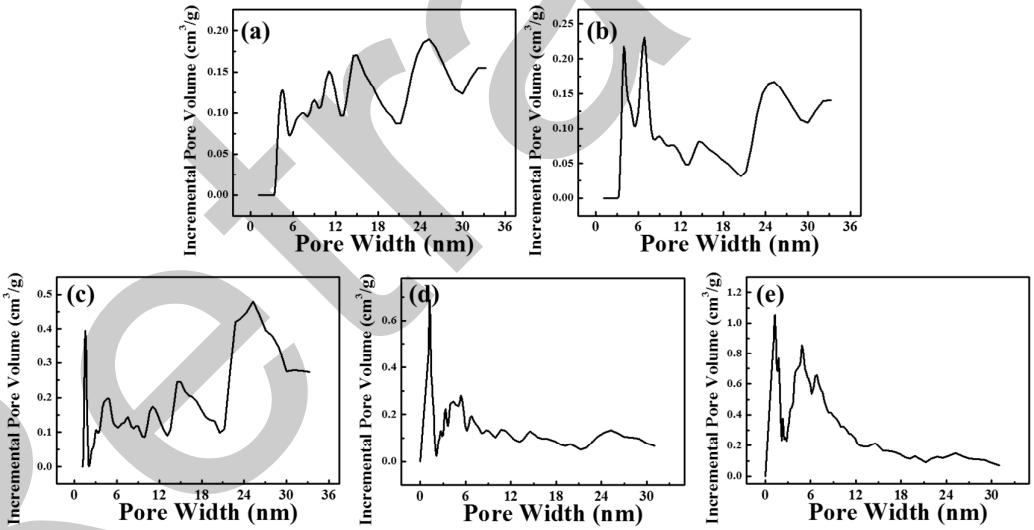

Figure S2 Nonlocal density functional theory (NLDFT) pore size distributions of COP materials by incremental pore volume. **(a)** COP-101; **(b)** COP-102; **(c)** COP-103; **(d)** COP-104; **(e)** COP-105.

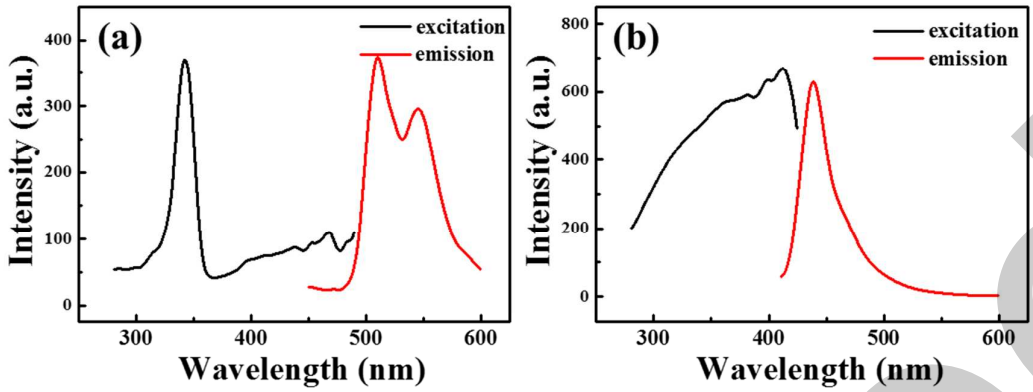

Figure S3 (a) and **(b)** are the excitation (black line) and emission (red line) spectra of the monomer DN and TBP, respectively.

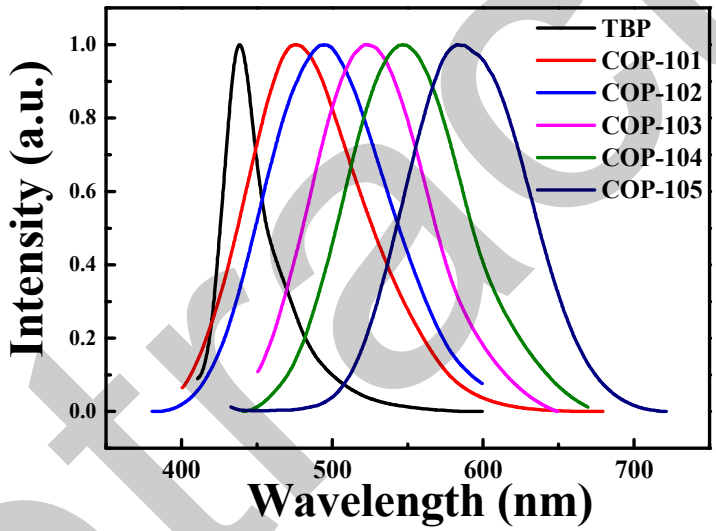

Figure S4 Normalized solid state PL emission spectra of TBP (black line), COP-101 (red line), COP-102 (blue line), COP-103 (pink line), COP-104 (green line) and COP-105 (purple line).

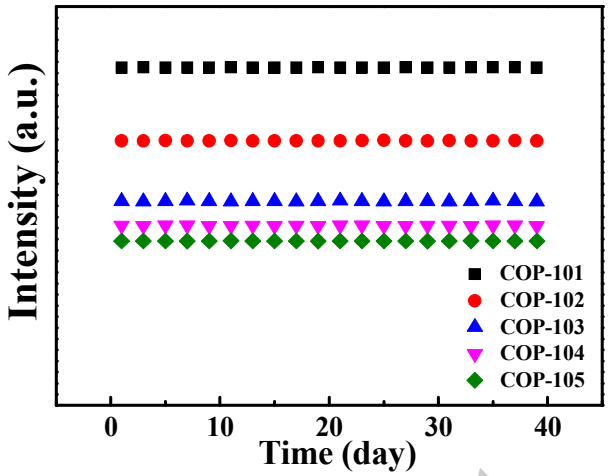

Figure S5 PL intensity of the COPs after different days.

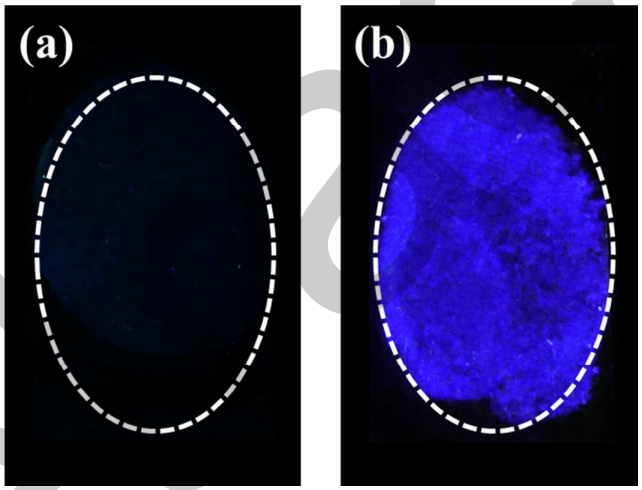

Figure S6 (a) and **(b)** are fluorescent images of LFPs after treated with the monomer DN and TBP, respectively.

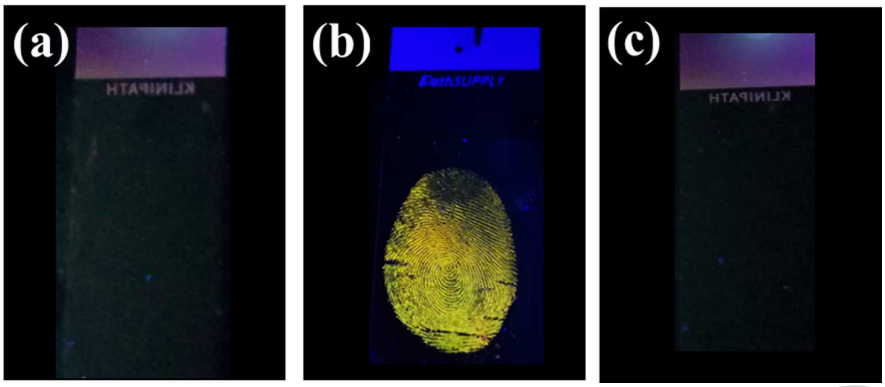

Figure S7 (a) The fluorescent image of the LFPs under an UV lamp (where λex=365 nm); **(b)** The fluorescent images of the LFPs after spraying the COP-104 under an UV lamp (where λex=365 nm); **(c)** The fluorescent images of the LFPs that press through the film after spraying the COP-104 under an UV lamp (where λex=365 nm).

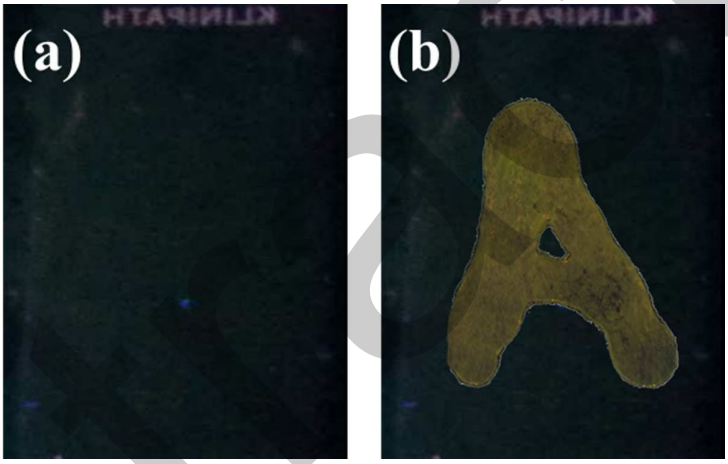

Figure S8 The fluorescent images after depositing squalene (10 ng) on the glass slides under an UV lamp (where λex=365 nm). **(a)** and **(b)** are before and after spraying COP-104, respectively.

Figure S9 The fluorescent images of LFPs deposited on glass slides by different people under an UV lamp (where λex=365 nm).

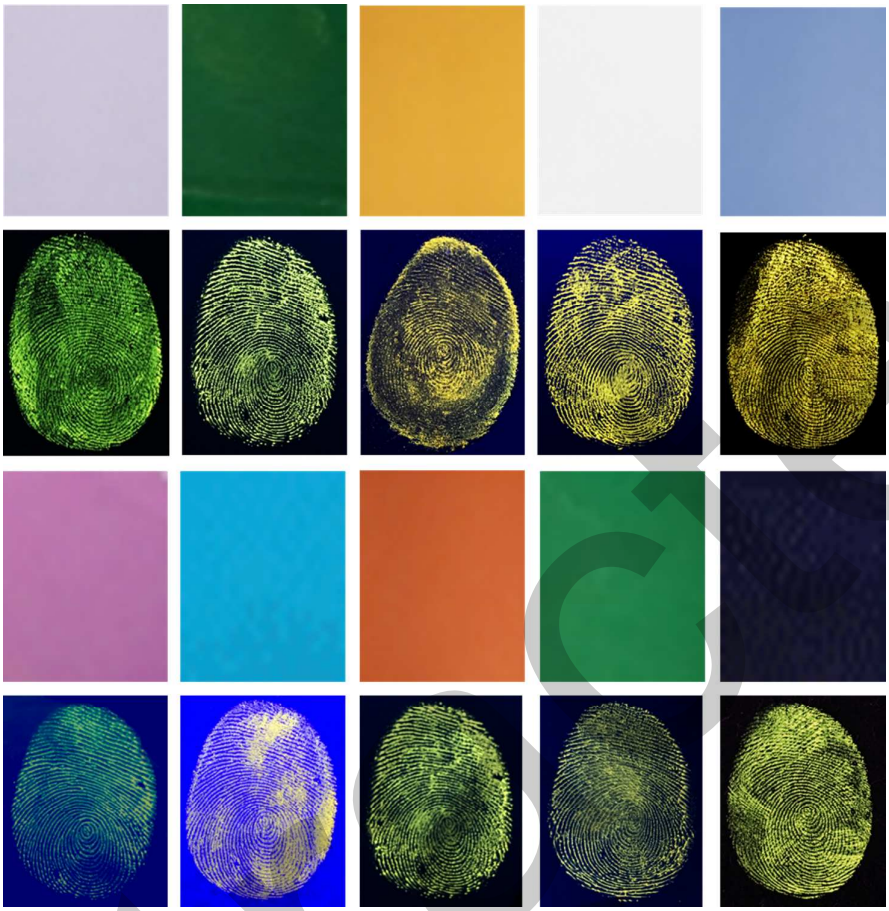

Figure S10 The fluorescent images of LFPs deposited on different color backgrounds under an UV lamp (where λex=365 nm).

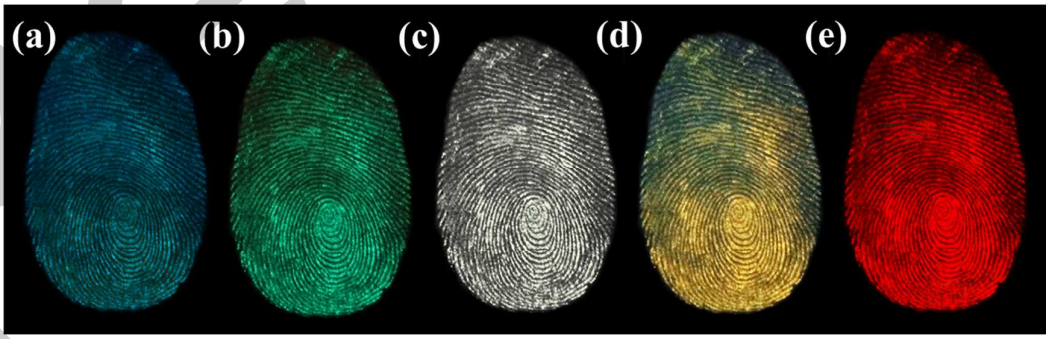

Figure S11 The fluorescent images of the aged LFPs which had been placed for 45 days. **(a)** ~ **(e)** are COP-101 ~ COP-105, respectively.

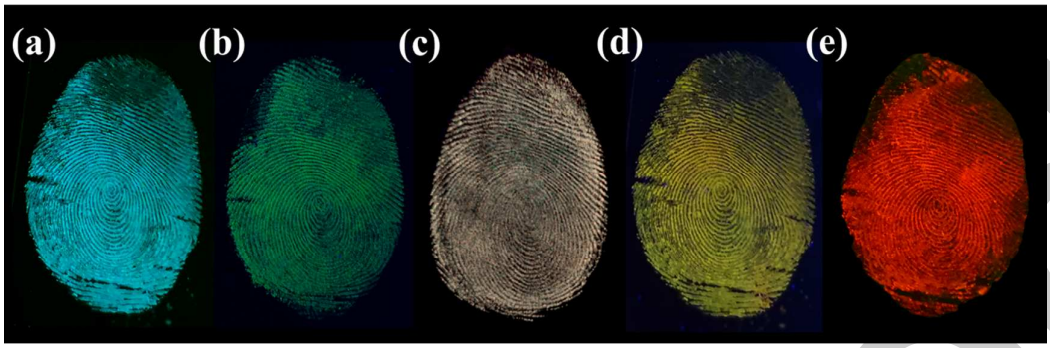

Figure S12 The fluorescent images of the LFPs that soak in water and shake for a few minutes. **(a)** ~ **(e)** are COP-101 ~ COP-105, respectively.