Electronic Supplementary Information (ESI)

Turn-on green fluorescence imaging for latent fingerprint applications

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CONTENTS

1. Experimental:

(a) Materials and instrumentation

Unless otherwise stated, all starting materials, reagents and solvents used in the experiment were purchased from Energy, Aladdin, Alfa Aesar, J&K and Sinopharm Chemical Reagent Co. Ltd.

^{1}H and ^{13}C NMR Spectroscopy. All experiments were performed on a 600 MHz Bruker AV 600 spectrometer at room temperature using DMSO-d_6 as the solvent.

UV-vis absorption and PL emission. The UV-Vis absorption and photoluminescence (PL) emission of the compounds were measured by Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600) and Edinburgh instruments (FLS 920 spectrometers), respectively.

(b) Synthesis procedures

Synthesis of compound 4-(4-(2-hydroxyethyl)piperazin-1-yl)benzaldehyde：

In a 50 mL glass bottle was added 2-(piperazin-1-yl)ethanol (2 g, 15.3 mmol), 4-fluorobenzaldehyde (1.906 g, 15.3 mmol), potassium carbonate (4.3 g, 31.2 mmol), water as a solvent, it was refluxed at a constant temperature of 100 °C for about 24 h, and the experiment was over. After cooling to room temperature, the mixture was extracted and separated in a separatory funnel using ethyl acetate and saturated aqueous sodium chloride solution, and then concentrated under reduced pressure to obtain a white solid product (3.2 g, 89% yield).^{1}H NMR (400 MHz, DMSO-d6) δ 9.71 (s, 1H), 7.75 – 7.66 (m, 2H), 7.09 – 7.00 (m, 2H), 4.47 (t, J = 5.4 Hz, 1H), 3.59 – 3.49 (m, 2H), 3.41 – 3.30 (m, 5H), 2.57 – 2.45 (m, 5H), 2.43 (t, J = 6.2 Hz, 2H).

Synthesis of PVPOH：

In a 50 mL round bottom flask was added 4-(4-(2-hydroxyethyl)piperazin-1-yl)benzaldehyde (500 mg, 2.13 mmol), 4-picoline (198.37 mg, 2.13 mmol), Potassium tert-butoxide (478.01 mg, 4.26 mmol), 10 ml of DMF. After reacting at 80°C for about 24 hours, the reaction was stopped. After the reaction flask was cooled to room temperature, it was extracted with dichloromethane, washed with n-hexane, and dried with anhydrous Na_2SO_4. The obtained solid was concentrated under reduced pressure and purified by silica gel column chromatography to finally obtain a yellow solid (compound PVPOH, yield 67%). ^{1}H NMR (600 MHz, Methanol-d4) δ 8.46 – 8.42 (m, 1H), 7.56 – 7.51 (m, 2H), 7.03 – 6.97 (m, 2H), 3.76 (t, J = 6.0 Hz, 1H), 3.31 (dd, J = 4.4, 2.5 Hz, 2H), 2.73 (t, J = 5.1 Hz, 2H), 2.63 (t, J = 6.0 Hz, 1H), 0.02 (s, 2H). 13C NMR (151 MHz, Chloroform-d) δ 151.64, 148.73, 146.83, 133.90, 128.01, 127.30, 121.70, 120.73, 115.23, 59.90, 58.41, 53.08, 48.16.

(c) The radiative and non-radiative rate constants

According to the obtained fluorescence quantum yield (φ_f) and fluorescence lifetime (τ_f) of the aggregated state of PVPOH molecules at room temperature, through Equation (2)-(3), the radiative rate constant (K_r) and non-radiative rate constant (K_{nr}) can be calculated to be 0.099 and 1.167, respectively."

$$K_r = \frac{\varphi_f}{\tau_f} \tag{1}$$

$$K_{nr} = \frac{1 - \varphi_f}{\tau_f} \tag{2}$$

2. NMR spectra and Mass spectra

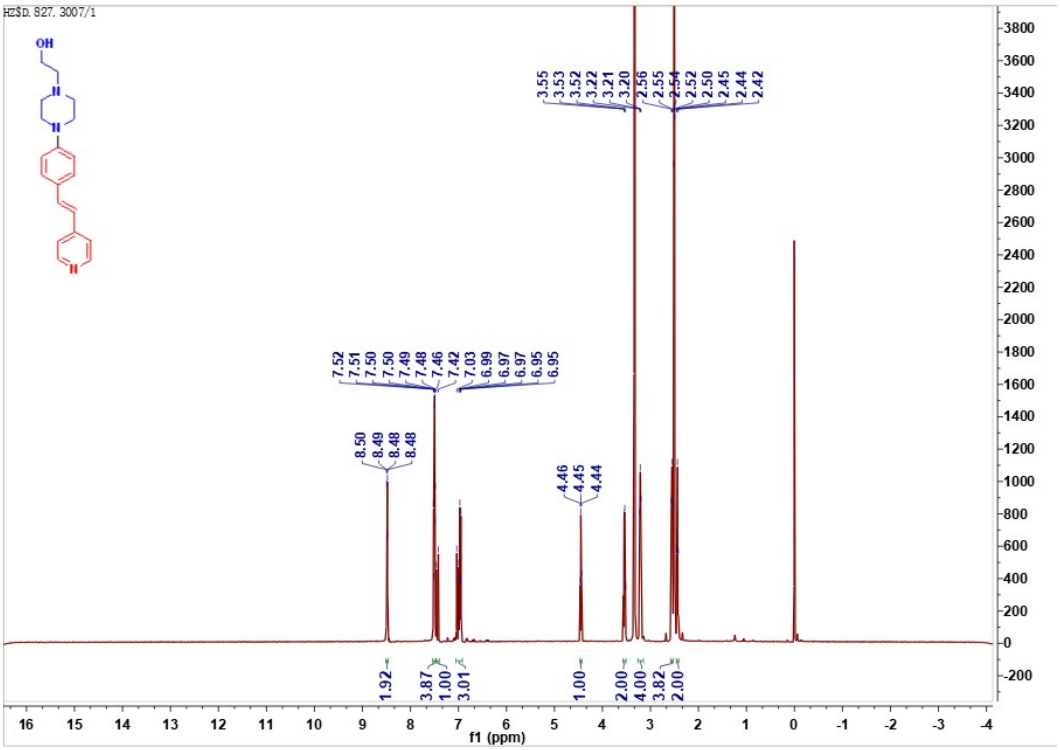


Figure S1. ^{1}H NMR spectra of PVPOH

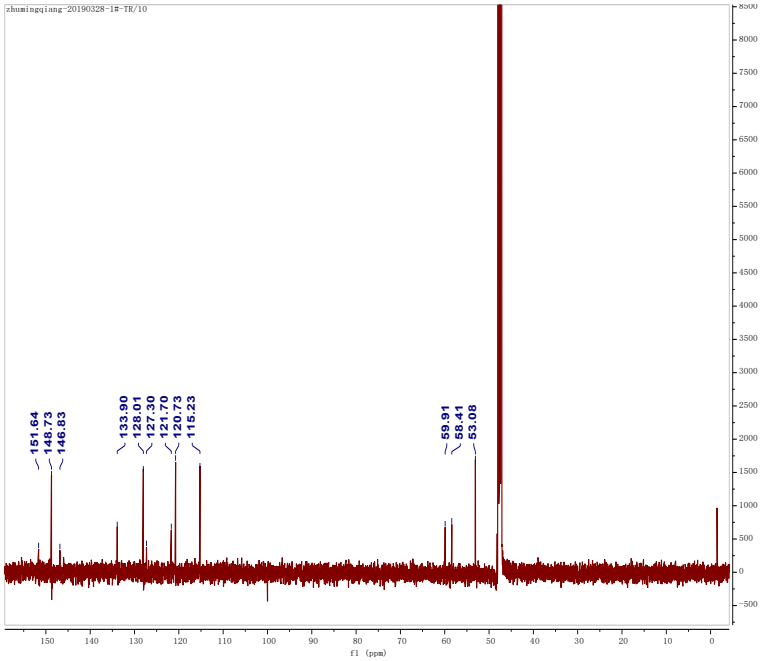


Figure S2. ^{13}C NMR spectra of PVPOH

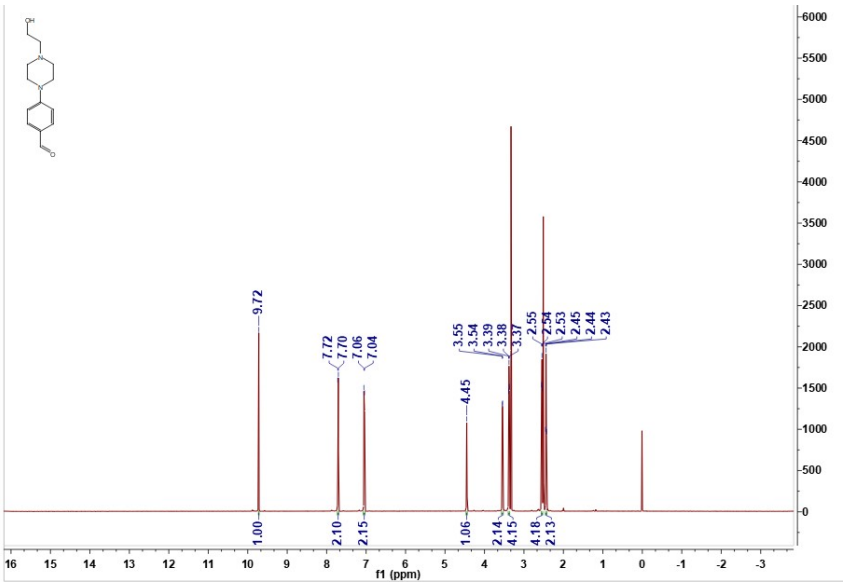


Figure S3. [1]H NMR spectra of compound 4-(4-(2-hydroxyethyl) piperazin-1-yl) benzaldehyde

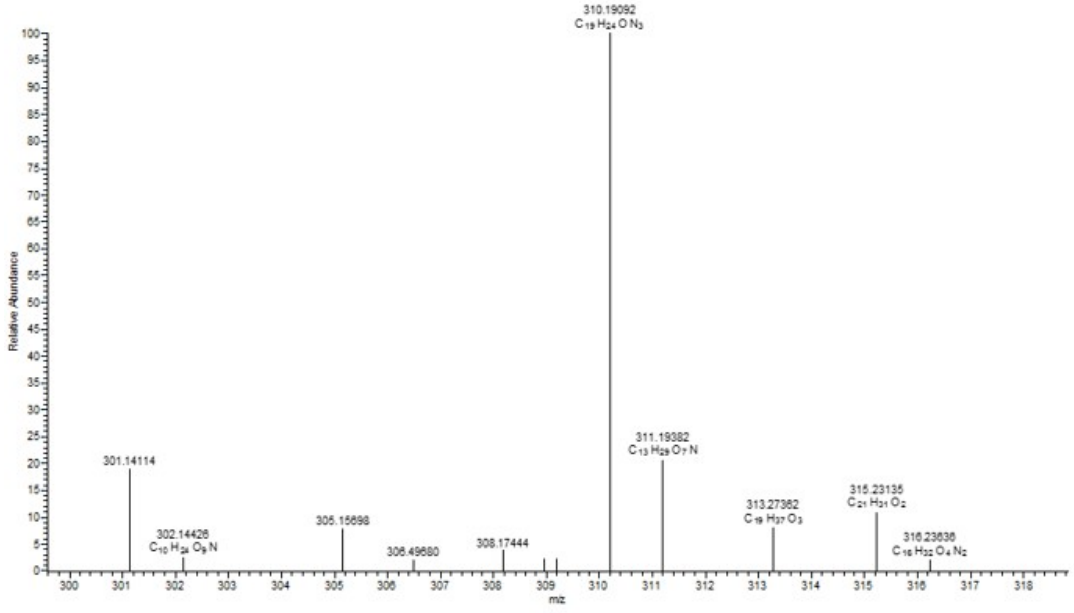


Figure S4. Mass spectra of PVPOH

3. Side view of optimized structure

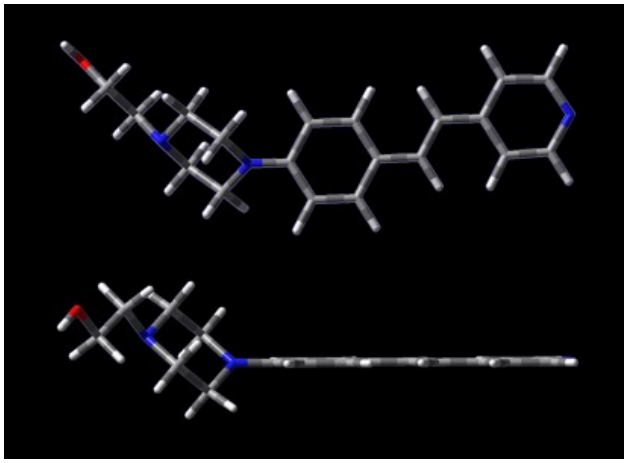


Figure S5. Side view of optimized structure of PVPOH

4. Density functional theory calculations

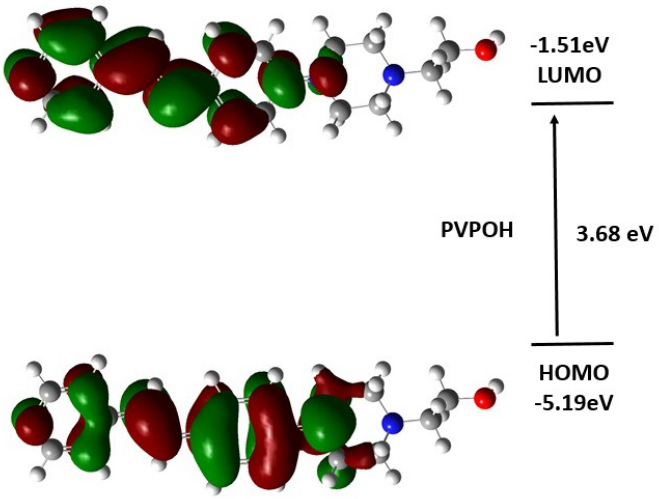
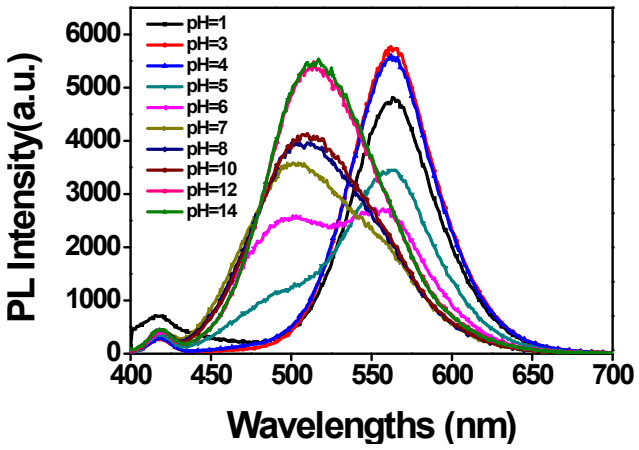
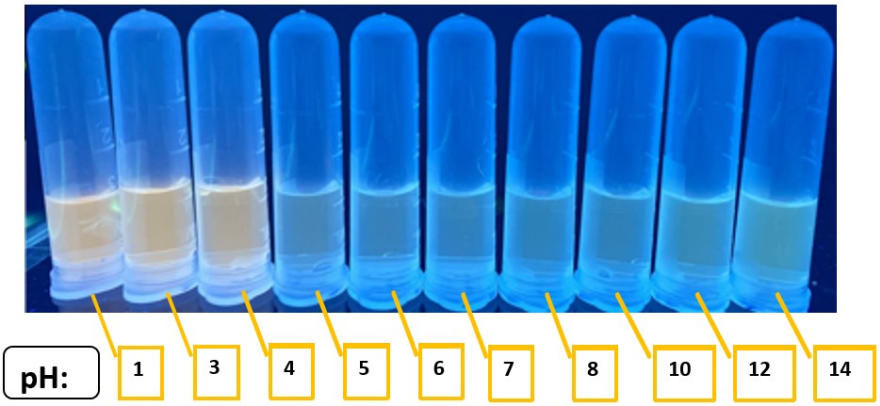


Figure S6. Simulation diagram of HOMO and LUMO electronic cloud distribution, Eg (energy gap) = LUMO – HOMO=3.68eV.

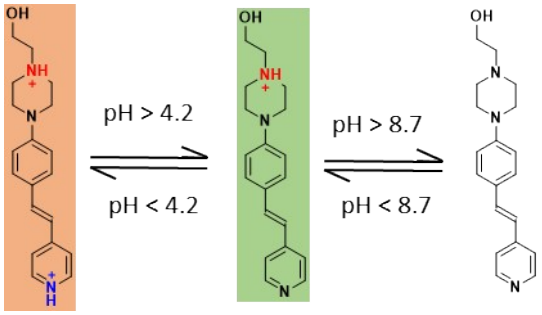
5. Normalized fluorescence emission spectra



(a)



(b)



(c)

Figure S7. The pH dependence of PVPOH fluorescence. (a) Fluorescent emission spectra of PVPOH molecules at pH= 1-14; (b) Fluorescent images of PVPOH at different pH values; (c) The plausible structures of PVPOH at various pH values.

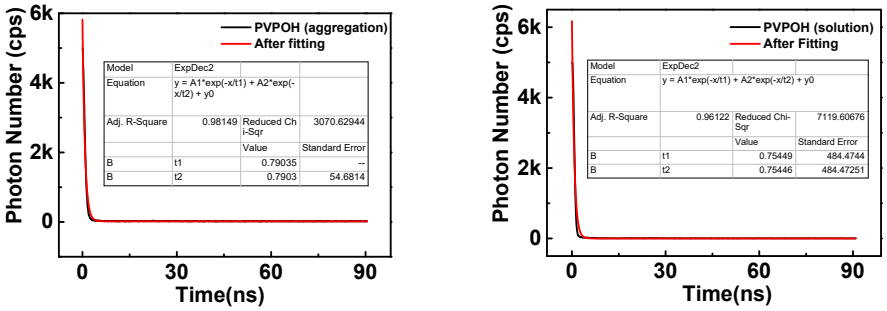
6. Viscosity table corresponding to PEG2000 solution

Table S1. Different viscosities of PEG2000 solutions with different mass ratios

composition	Proportion	temperature	Viscosity（mP×s）
PEG2000+PBS*1	0%	25℃	2.7
PEG2000+PBS*1	5%(10g/190ml)	25℃	4.5
PEG2000+PBS*1	15%(30g/170ml)	25℃	9.9
PEG2000+PBS*1	25%(50g/150ml)	25℃	18.6
PEG2000+PBS*1	35%(70g/130ml)	25℃	33.9
PEG2000+PBS*1	45%(90g/110ml)	25℃	65.4
PEG2000+PBS*1	55%(110g/90ml)	25℃	134.7
PEG2000+PBS*1	65%(130g/70ml)	25℃	286.7

7. Fluorescence lifetime diagram

The fluorescence lifetime of the PVPOH molecule in the aggregated state and in solution is 0.79 ns and 0.75 ns, respectively.



(a) (b)

Figure S8. Fluorescence lifetime diagram of PVPOH molecules. (a) aggregated in PEG 60% viscous solution. (b) in PBS buffer solution (excitation wavelength is 365 nm)

8. SEM image of PVPOH aggregated dots

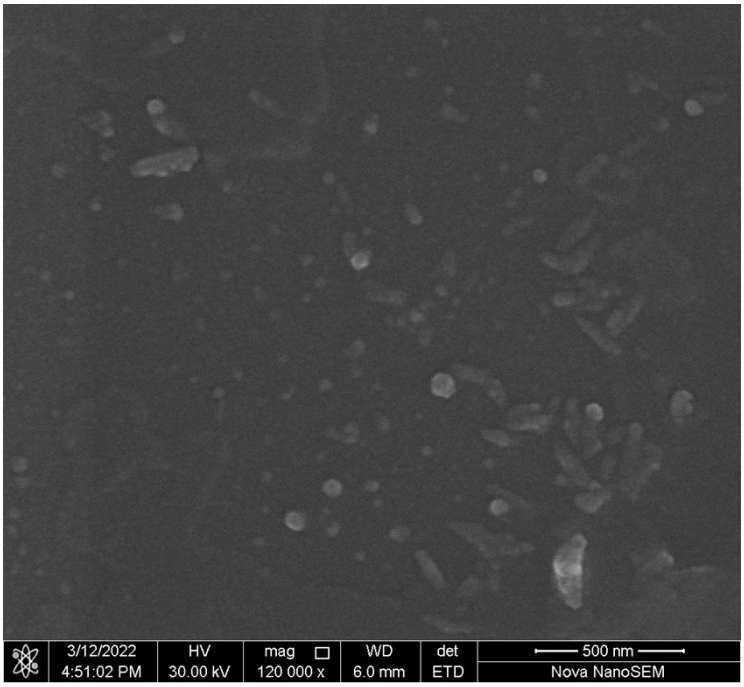


Figure S9. SEM image of PVPOH aggregated dots.

9. Comparison of fingerprint imaging effects of different concentrations of PVPOH solutions

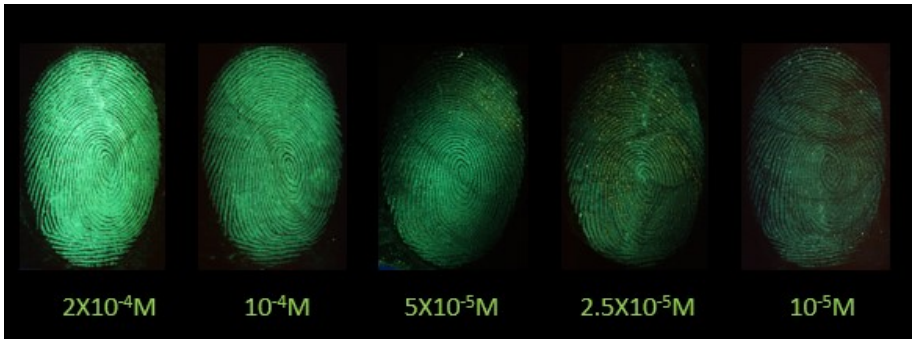


Figure S10. Comparison of the effects of different concentrations of PVP solutions on fingerprint imaging，10^{-4} M is the best. (Fluorescence darkfield microscope camera)

10. Summary table of materials currently used for green fluorescence imaging of fingerprints

Table S2. the current materials for green fluorescent imaging of fingerprints

No.	Type	Mater.	Ex. (nm)	method	level of detail	Re.	substrates	P.S.
1	Quantum dots	Multicolored water-soluble CdTe QDs	365	solution method (water)	1−2 levels	[14]	smooth and blue object	
2	Quantum dots	the PAA-functionalized green QDs and red QD-doped silica nanoparticles (ZnCdS QDs)	365	powder method (silica nanoparticles）	1−2 levels	[15]	several nonporous surfaces; glass and paper.	
3	Carbon quantum dots	Carbogenic nanoparticle powder	395	powder method	1−2 levels	[8]	glass slide; soft drink bottle foil	
4	Carbon quantum dots	phenyl-doped g-C_3N_4 powder	365	powder method	1−3 levels	[10]	Porous smooth inorganic materials ; nonporous metals and colorless polymers ;different color substrates; and autofluorescent substrates	Dust hazard with powder method
5	Carbon quantum dots	N-doped CDs	366	solution method	1−2 levels	[9]	filter paper	
6	Upconverting nanoparticles	Ho^{3+}-activated NaYbF4 UCNPs	980	powder method	1−2 levels	[12]	Glass; plastic Petri dish and coin	

7	up/downconversion luminescent powders	β-$NaYF_4$:RE^{3+} phosphors	254, 980	powder method	1−2 levels	[11]	plastic culture dish; glass slide; metal key and document envelope	
8	Upconversion Fluorescent Nanoparticles	$NaYF_4$:Yb,Er UCNPs	980	powder method	1−2 levels	[13]	those with a single background color; multiple background colors and strong background autofluorescence smooth substrates	
9	AIE Materials	diphenylpyrimidinone–salicylideneamine derivatives DPPS-1 and DPPS-2	365	solution method (CH_3CN /water mixture)	1−2 levels	[23]	Glass; aluminium; stainless steel; ceramic tile and currency metal coin	
10	AIE Materials	AIEE-active conjugated polyelectrolyte PFTPEBT-MI	365	solution method (Immerse in the solution for 1min)	1−3 levels	[21]	Glass; aluminum foil; steel; coins; adhesive tape	Immersion method is not suitable for large area imaging; methanol is added to the spray method to assist drying.