Supporting Information

Synthesis and properties of novel fluorescent organogel: AIE, GO hybrid functional gel, and multi-stimuli responsiveness

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Contents

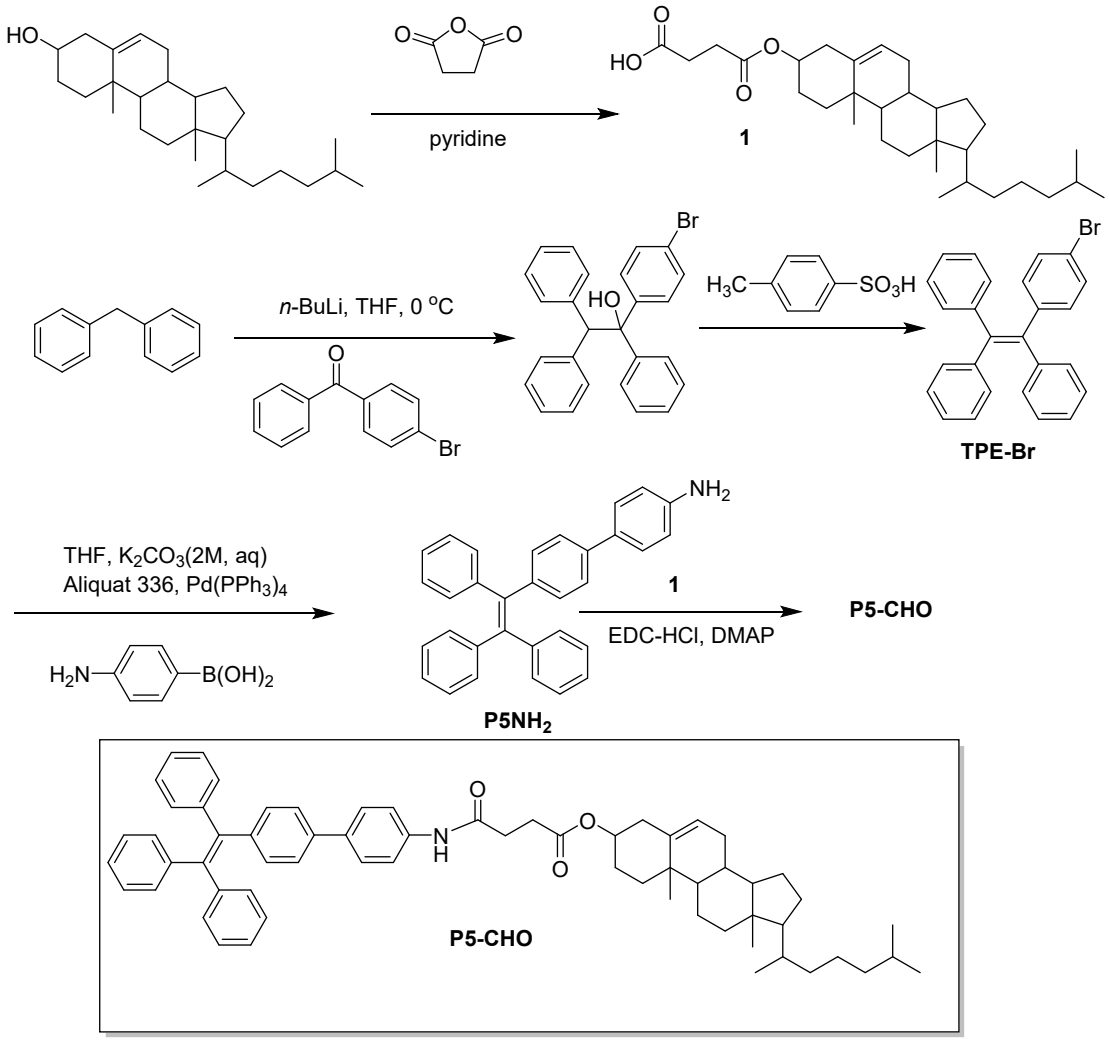
Synthesis and characterization

2.1 Materials and instruments

4-Aminophenylboronic acid, 4-bromophenyl phenylmethanone, diphenylmethane, cholesterol, succinic anhydride, 2,4-d ihydroxybenzaldehyde, n-butyl lithium, aliquat 336, tetrakis (triphenylphosphine) palladium (0) were purchased from Aladdin company and used as received. 4-dimethylamiopryidine (DMAP), 4-toluene sulfonic acid,1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl) were purchased from Shanghai Darui company (China) used as received. Ultra-pure water was used in the experiments. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. All other reagents and solvents were purchased as analytical grade from Zhangjiang Kangbai Company (China) and used without further purification. 1-bromo-4-(1,2,2-triphenylvinyl)benzene (TPE-Br)[1], and 4'-(1,2,2-triphenylvinyl)biphenyl-4-amine (P_5NH_2)[1-2] were prepared according to the literature methods.

The IR spectra were measured on a Nicolet-6700 FT-IR spectrometer by incorporating the samples in KBr disks. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}CNMR) spectra were measured on a Bruker AVANCE III spectrometer [$CDCl_3$, tetramethylsilane (TMS) as the internal standard]. The electronic spray ionization (ESI) high-resolution mass spectra were tested on a HP 5958 mass spectrometer. The SEM images were obtained using a Hitachi S-4800 spectrometer. The UV/Vis spectra were determined on a Shimadzu-2550 spectrophotometer. Wide-angle X-ray diffraction (WAXD) measurement was performed by using a Philips X'Pert Pro diffractometer with an X-ray source of Cu Ka (λ=0.15406 nm) at 40 kV and 40 mA, at scan rates of 4 °per 1 min. Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer at a heating rate of 10 ^{o}C/min under N_2 atmosphere. Photoluminescence spectra (PL) were measured on a Cary Eclipse spectrometer with 5 nm and 5 nm slit widths for excitation and emission, respectively. The THF/water mixtures with different water fractions were prepared by slowly adding

distilled water into the THF solution of samples under ultrasound at room temperature. Pressed samples were prepared by pressing in an IR pellet at 1500 psi for 5 min. Annealing experiments were done on a hot-stage with automatic temperature control system for 5 min, the annealing temperatures was 164 °C. The experiment of solvent vapor fuming treatment was performed by filling the pressed sample on a grooved glass slide, which was then placed in a large beaker saturated with CH_2Cl_2 vapor for 5 min at room temperature.



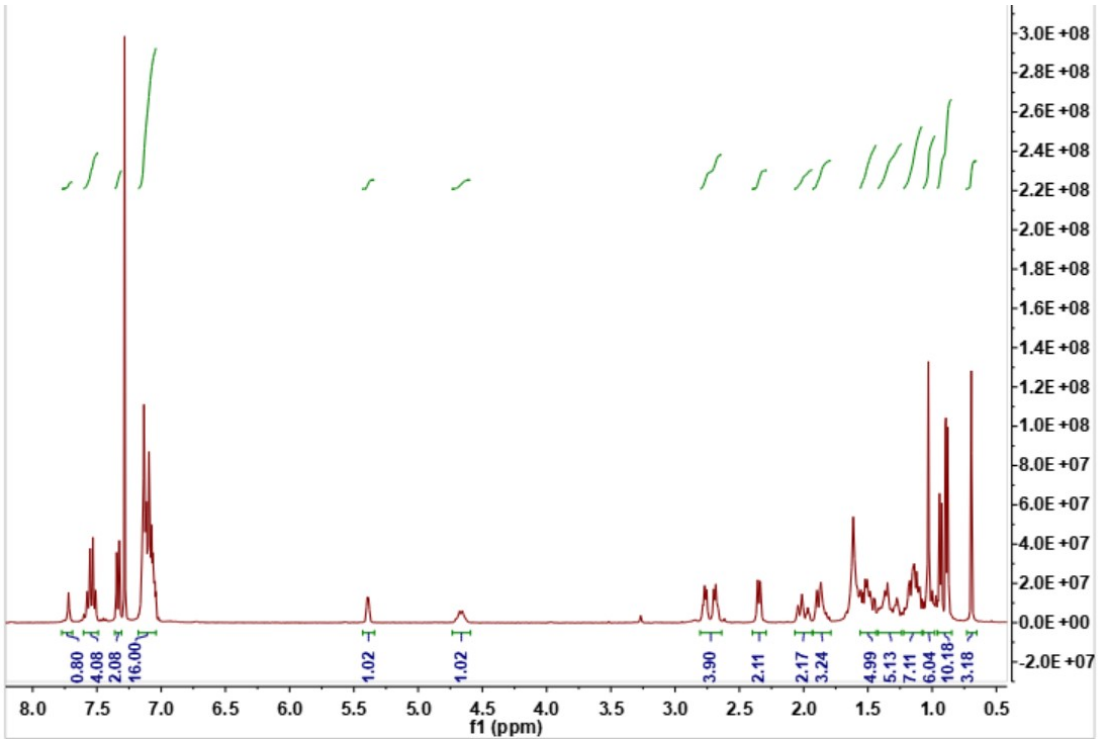
Scheme S1. Synthetic routes for **P5-CHO**

2.2 Synthesis of 3-Cholesteryloxycarbonylpropanoic acid (1):

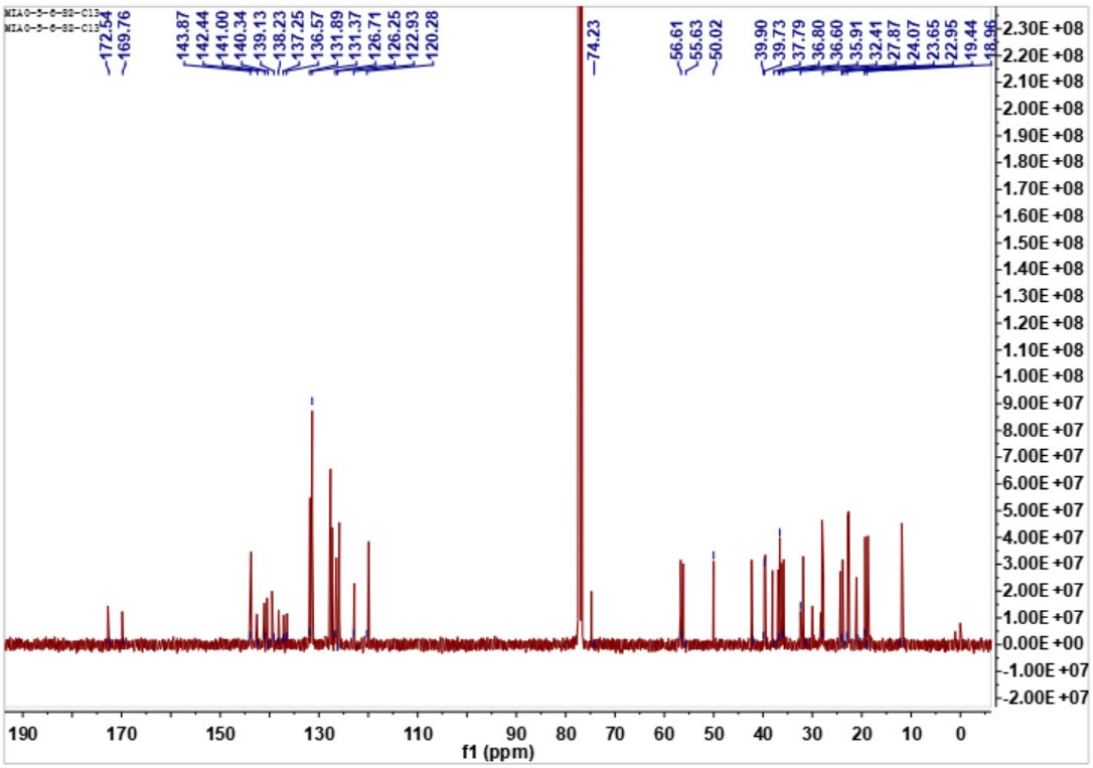
A solution of cholesterol (5.80 g, 15 mmol), succinic anhydride (1.50 g, 15 mmol), pyridine (1.00 mL), and dry heptane (150 mL) were heated to reflux for 21 h and cooled to room temperature. The resulting precipitate was recrystallized twice from acetone. Yield: 70%.

2.3 Synthesis of P5-CHO

P_5NH_2 (0.20 g, 0.47 mmol) and **1** (0.26 g, 0.54 mmol) were dissolved in THF (50 mL), and then EDC-HCl (0.01 g) and DMAP (0.01 g) were added. The solution was stirred at room temperature for 12 hours. After removing the solvent under reduced pressure, the residue was crystallized from ethanol to give white crystalline powder **P5-CHO** (0.31 g, 73.8% yield). IR (KBr): υ=3434 cm^{-1}(N-H), 2942 cm^{-1} (-CH_2-), 2867 cm^{-1} (-CH_3), 1731 cm^{-1} (C=O at COOR), 1699 cm^{-1} (C=O at RCONHR'), 1671 cm^{-1} (C=C), 1598, 1528, 1497 cm^{-1} (phenyl); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.54 (q, J = 8.8 Hz, 4H), 7.34 (d, J = 8.3 Hz, 2H), 7.17 – 7.03 (m, 16H), 5.39 (d, J = 3.8 Hz, 1H), 4.74 – 4.60 (m, 1H), 2.73 (dt, J = 12.1, 5.8 Hz, 4H), 2.35 (d, J = 7.8 Hz, 2H), 2.01 (t, J = 15.5 Hz, 2H), 1.88 (d, J = 11.1 Hz,3H), 1.55 – 0.84 (m, 33H), 0.70 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75MHz) δ (ppm): 172.5, 169.8, 143.9, 142.4, 141.0, 140.3, 139.1, 138.2, 137.3, 136.6, 131.9, 131.4, 126.7, 126.3, 122.9, 120.3, 74.2, 56.6, 55.6, 50.0, 39.9, 39.7, 37.8, 36.8, 36.6, 35.9, 32.4, 27.9, 24.1, 23.7, 22.9, 19.4, 19.0, 12.1; MALDI-TOF MS (ES+): m/z 892.5665 ($[M+H]^+$, calcd for $C_{63}H_{73}NO_3$, 891.5590).



^{1}H NMR of **P5-CHO**



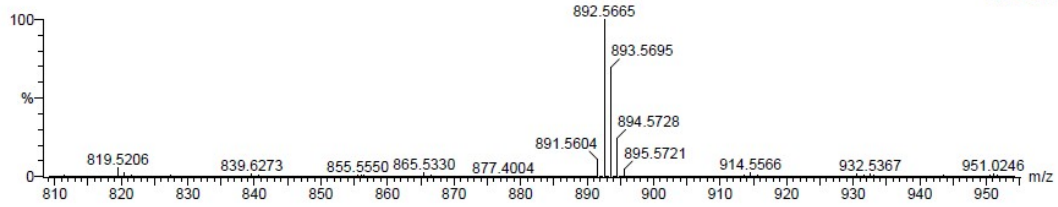
^{13}C NMR of **P5-CHO**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
69 formula(e) evaluated with 4 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-70 H: 0-80 N: 0-4 O: 2-3

X-MA ECUST institute of Fine Chem 21-Apr-2016 23:20:06
MX-WJ-04 54 (0.422) Cm (35:55) 1: TOF MS ES+ 9.49e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
892.5665	892.5669	-0.4	-0.4	27.5	147.9	0.0	C63 H74 N O3

HR-MS of **P5-CHO**

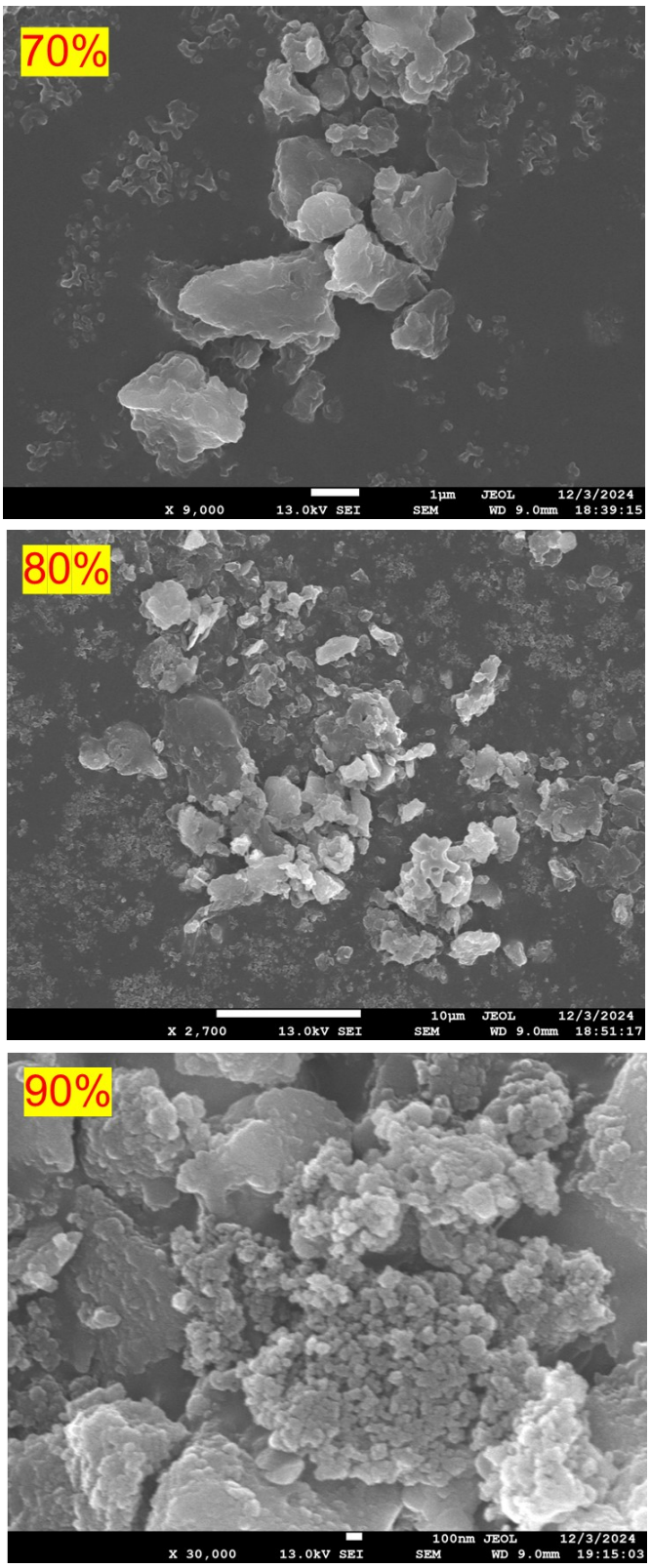


Figure S1 SEM images of **P5-CHO** prepared from different water fractions in THF/water mixtures.

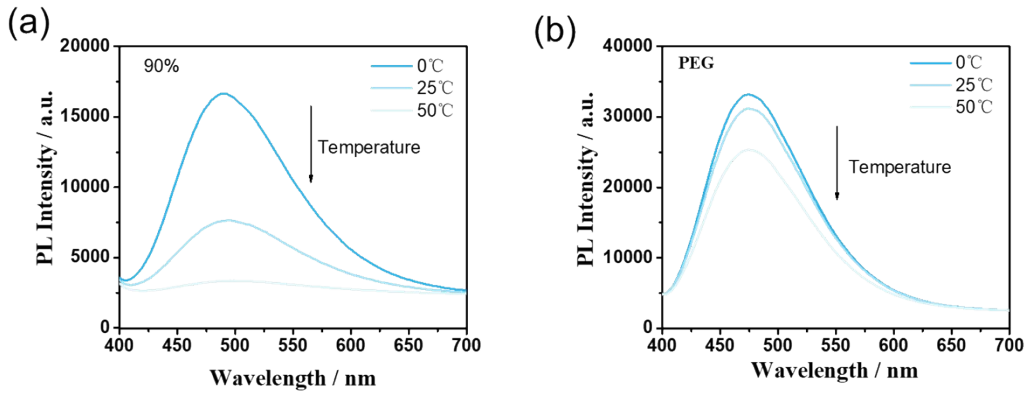


Figure S2 PL spectra of **P5-CHO** in f_{water} =90% (v/v, THF/water mixture) and polyethylene glycol (PEG) with different temperature (λ_{ex} = 365 nm), the concentration of **P5-CHO** is 2.5×10^{-5} mol/L, the concentration of PEG is 0.1g/mL.

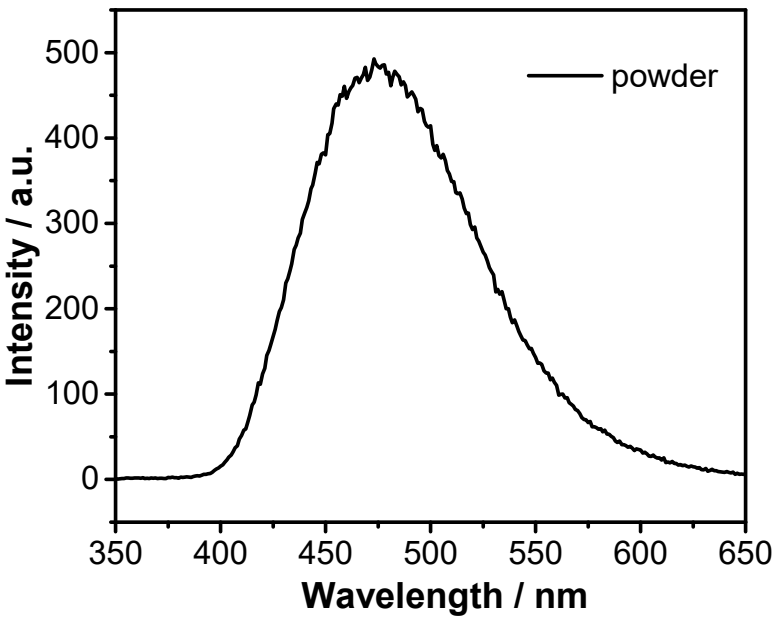


Figure S3 PL spectra of **P5-CHO** in solid powder.

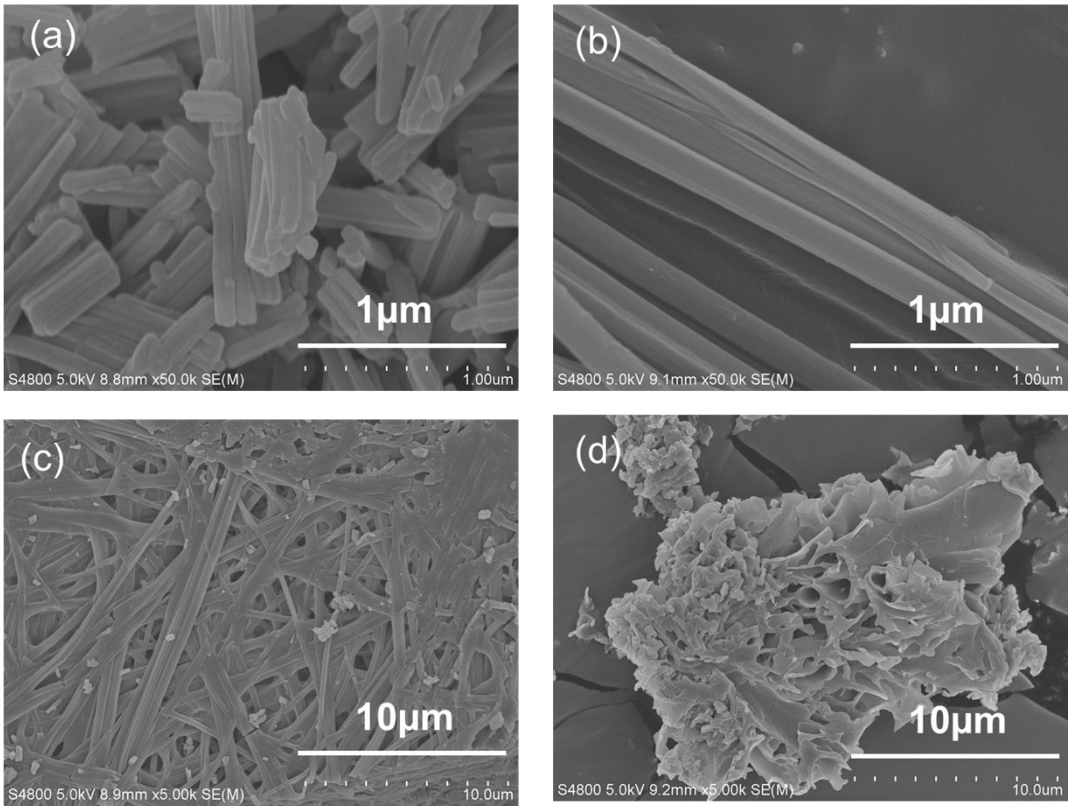


Figure S4 SEM image of xerogel prepared from different solutions for **P5-CHO**, (a) cyclohexane, (b) acetone, (c) DMF, (d) DMSO.

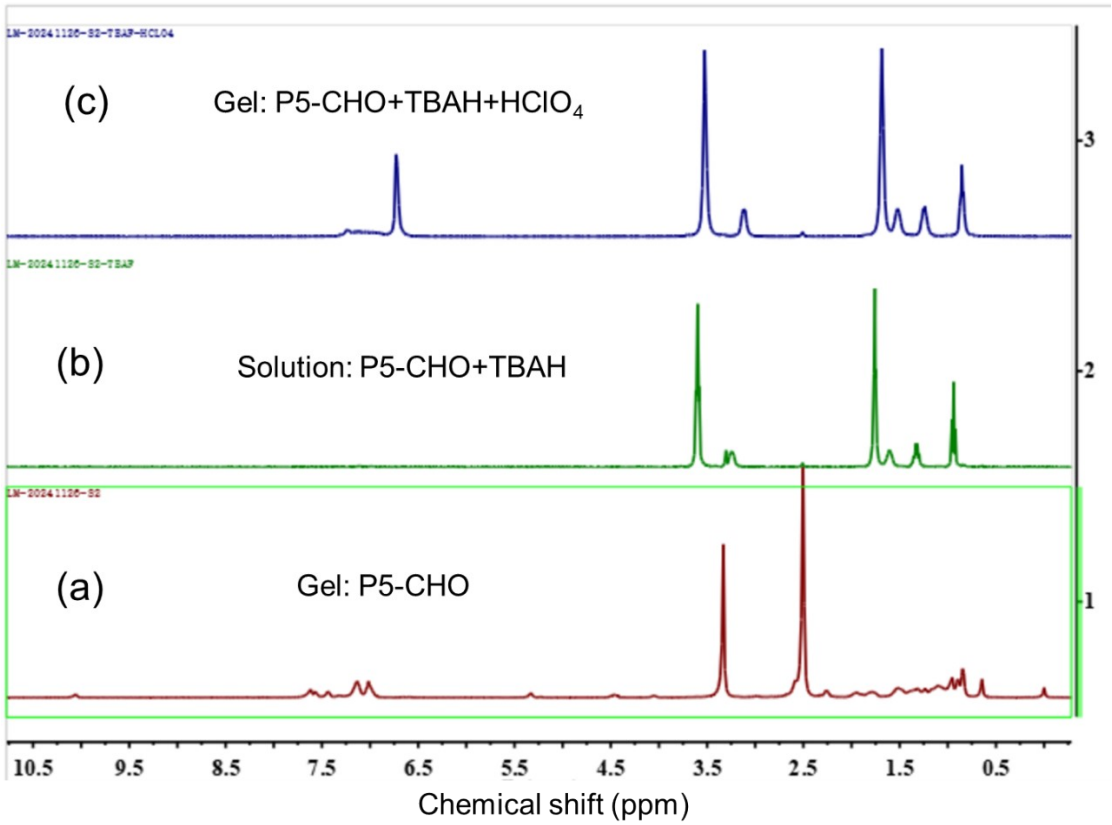


Figure S5 ^{1}H NMR of **P5-CHO** in different conditions, solvent: DMSO-d6, (a) gel of P5-CHO: add 0.55mL deuterated DMSO to 10 mg **P5-CHO**, heat to dissolve, and then stand to obtain gel, (b) add 3 drops of 1mol/L tetrabutylammonium fluoride solution to (a) to obtain solution, (c) then add 2 drops of $HClO_4$ to solution(b) to form gel.

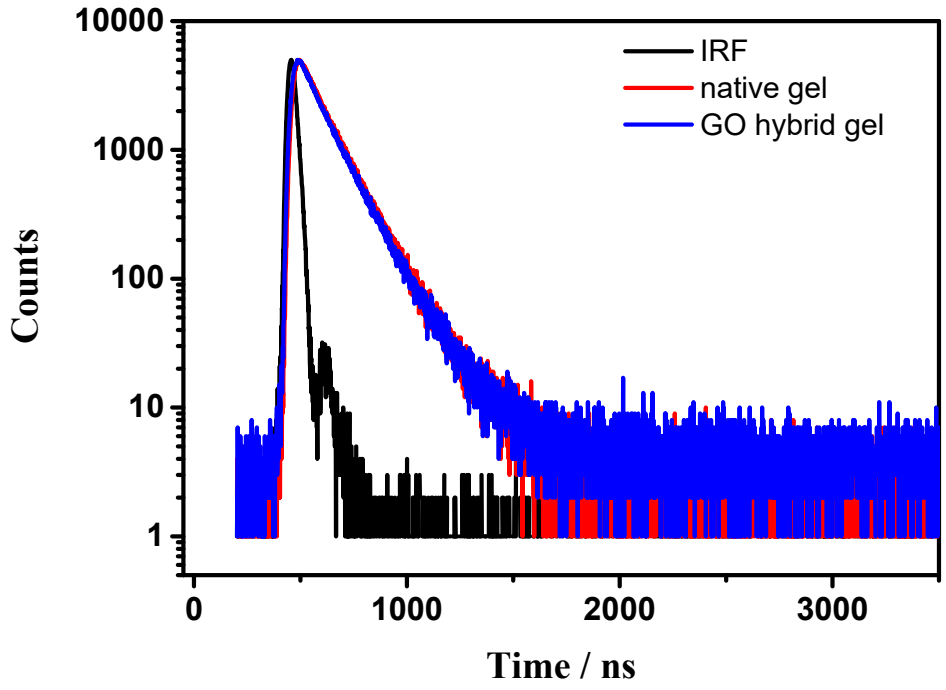


Figure S6 Time-resolved emission decay curves of native gel and GO-hybrid gel of **P5-CHO**.

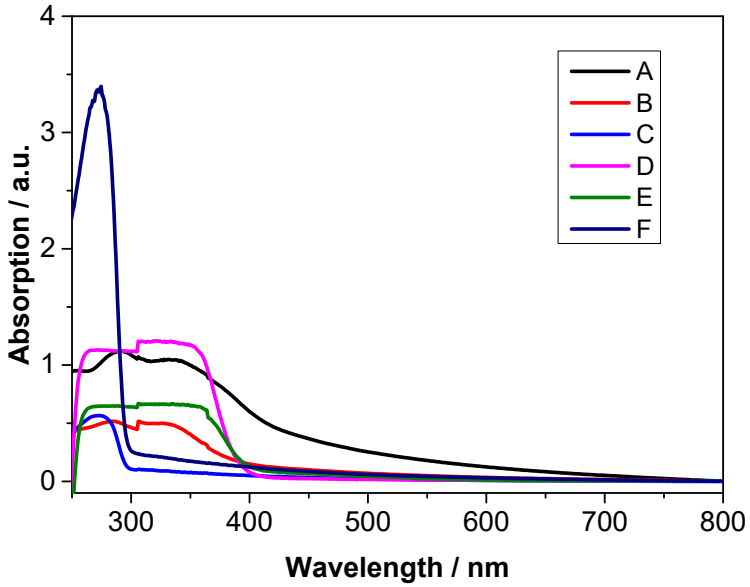


Figure S7 UV-vis absorption spectra of hybrid gel system in different states, (A) gel in DMSO, (B) GO-hybrid gel in DMSO, (C) GO dissolved in DMSO, (D) gel in DMF, (E) GO-hybrid gel in DMF, (F) GO dissolved in DMF.

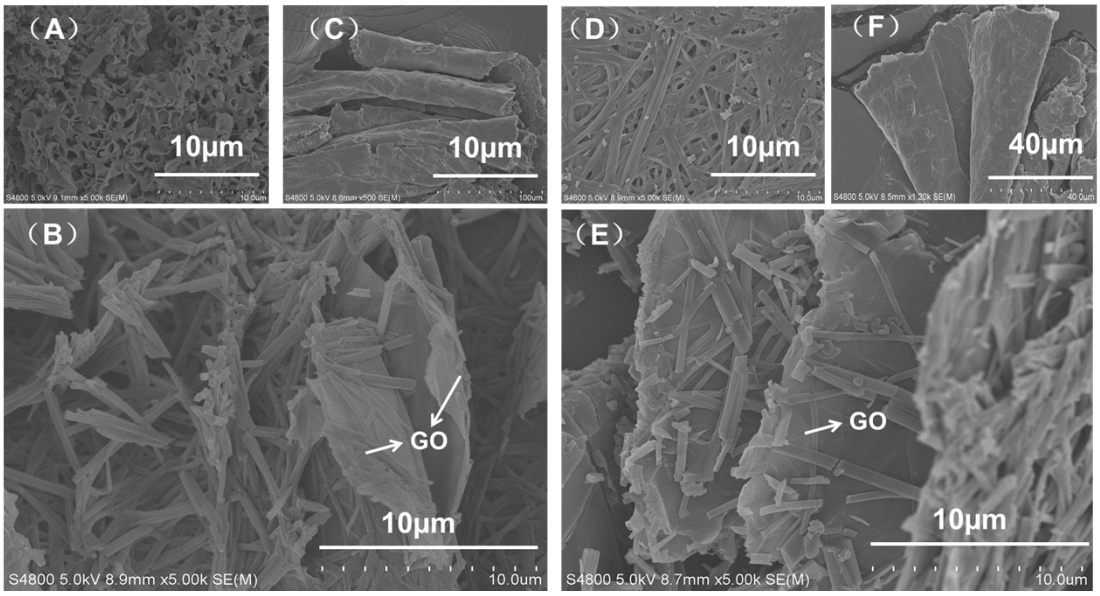


Figure S8 SEM image of xerogel prepared from different solutions for **P5-CHO**, (A) gel in DMSO, (B) GO-hybrid gel in DMSO, (C) GO dissolved in DMSO, (D) gel in DMF, (E) GO-hybrid gel in DMF, (F) GO dissolved in DMF.

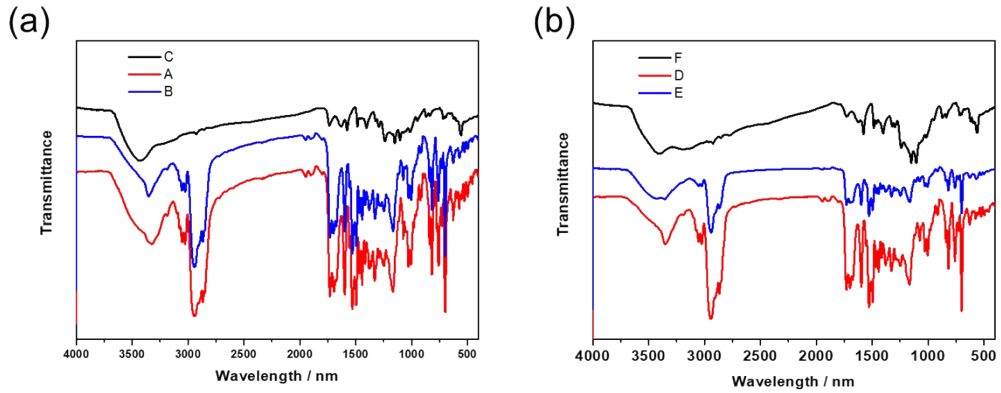


Figure S9 FTIR spectrum of xerogel prepared from different solutions for **P5-CHO**, (A) gel in DMSO, (B) GO-hybrid gel in DMSO, (C) GO dissolved in DMSO, (D) gel in DMF, (E) GO-hybrid gel in DMF, (F) GO dissolved in DMF.

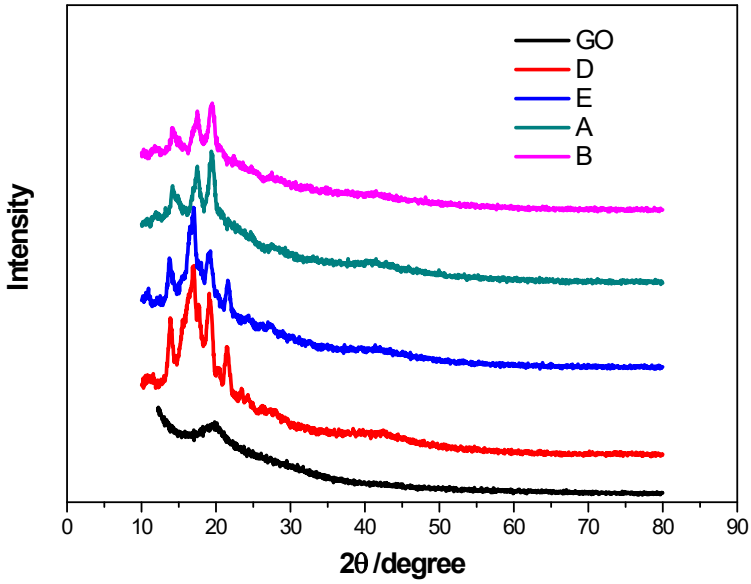


Figure S10 XRD spectrum of xerogel prepared from different solutions for **P5-CHO**, (A) gel in DMSO, (B) GO-hybrid gel in DMSO, (D) gel in DMF, (E) GO-hybrid gel in DMF.

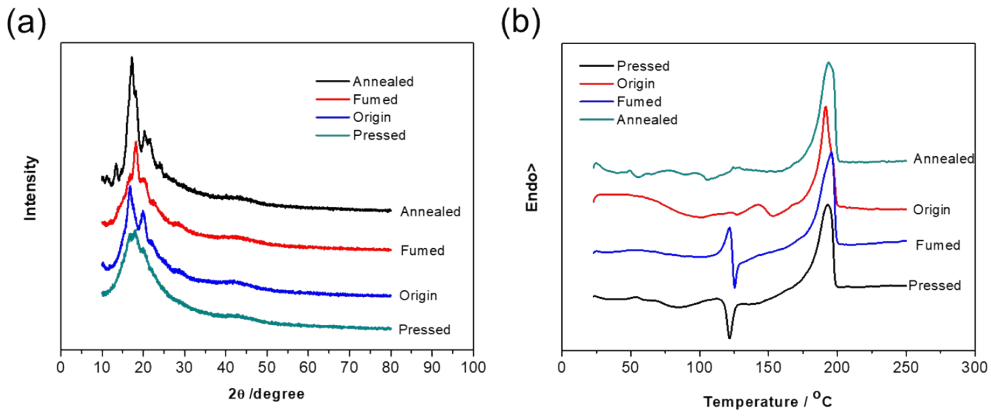


Figure S11 WAXD curves (A) and normalized PL curves (B) of compound **P5-CHO** under the different conditions: origin, fumed (vapor the pressed sample in CH_2Cl_2 for 5 min), pressing and annealing (heating the pressed sample at 164 °C for 5 min).

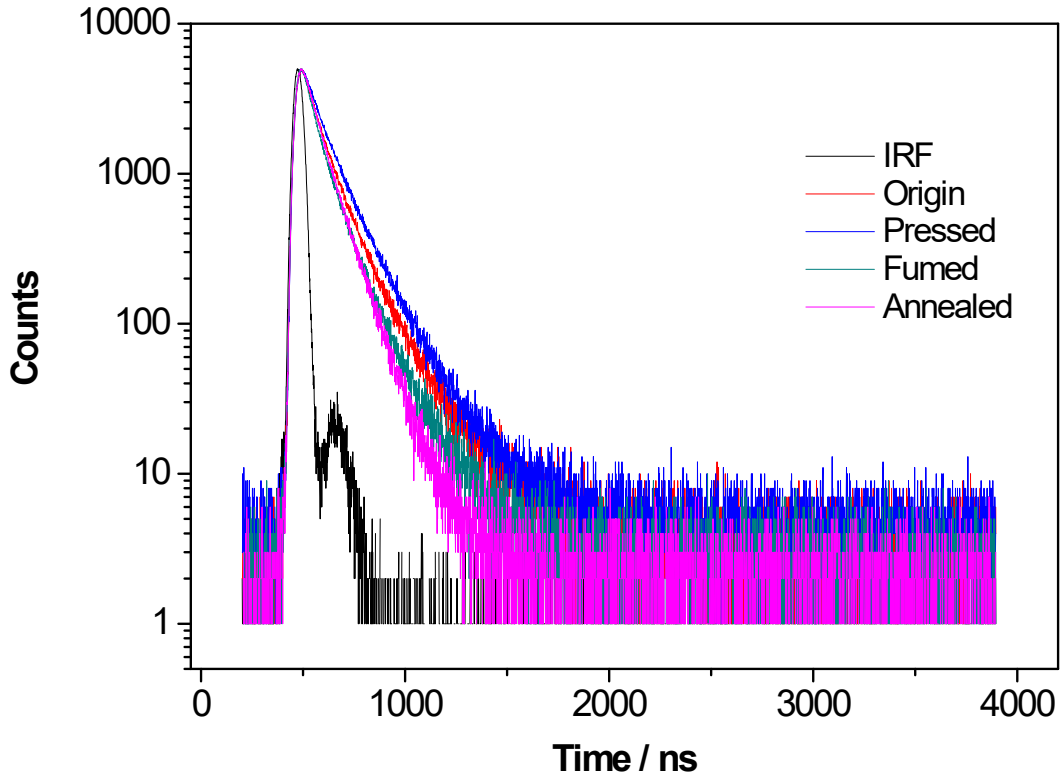


Figure S12 Time-resolved emission decay curves of compound **P5-CHO** under different treatment conditions.

Table S1 the relation of the CGC and the GO concentration in DMF and DMSO.

in DMF		in DMSO	
GO (mg/mL)	CGC (mg/mL)	GO (mg/mL)	CGC (mg/mL)
2.0	101.1	2.0	101.2
4.0	51.5	4.0	68.3
6.0	34.0	6.0	51.0

Table S2 Solid-state fluorescence lifetime data of **P5-CHO** under different conditions.

Sample	λ_{em}(nm)	τ (ns)
Origin	473	3.23
Pressed	495	3.72
Fumed	473	2.73
Annealed	473	2.64

Table S3 the photoluminescence quantum yield (PLQY) data of **P5-CHO** under different conditions.

Sample	PLQY(%)
Origin	32.23
Pressed	44.89

References

1. M. Luo, X. Zhou, Z. Chi, S. Liu, Y. Zhang and J. Xu, *Dyes Pigments*, 2014, **101**, 74-84.
2. M. Luo, Y. Liu, J. Zhao, L. Jiang, X. Chen, W. Li, Z. Yang, Q. Yan, S. Wang and Z. Chi, *Dyes Pigments*, 2022, **202**, 110222.