
Supporting Information

Covalent Organic Polymers with Solid-State Dual-Color Fluorescence Tunable by Ultraviolet Irradiation

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Experimental Procedures

1. Materials and instruments

1.1. Reagents

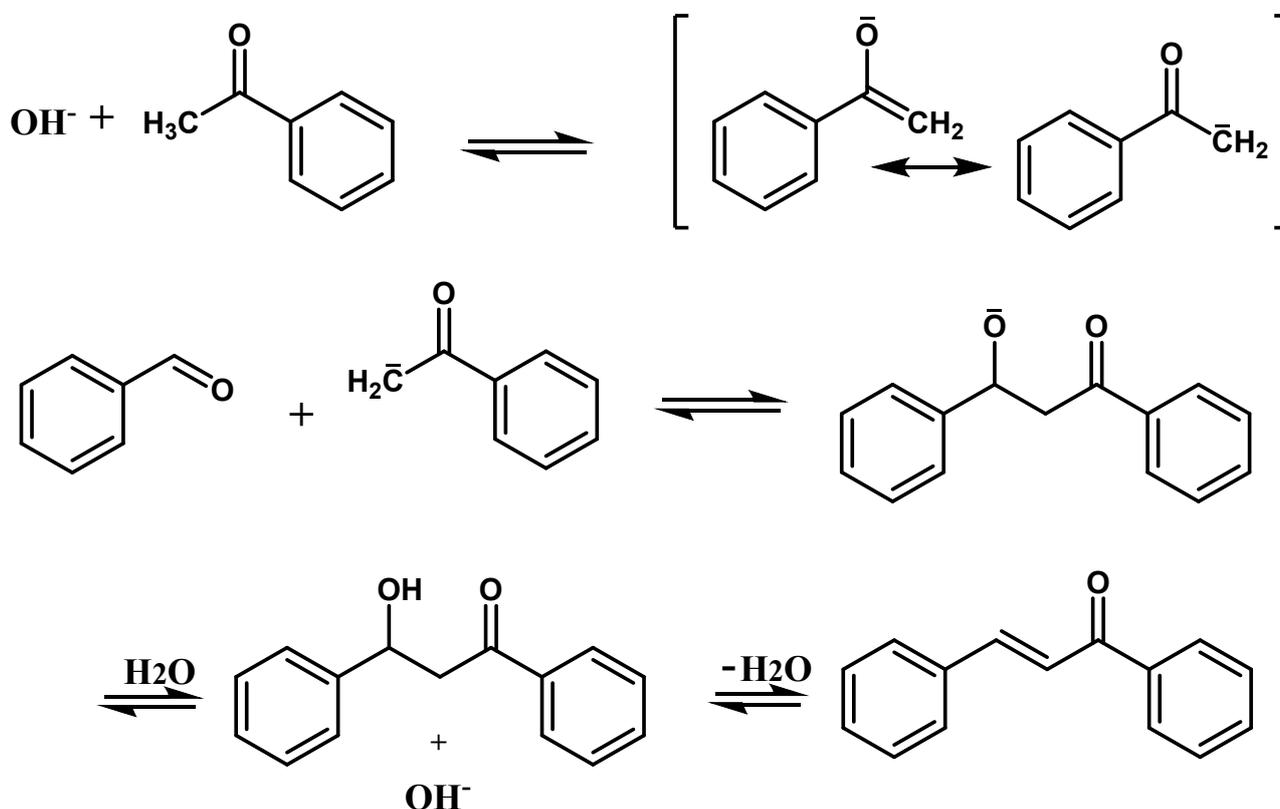
All the chemicals were purchased from commercial sources, and used without further purification. 1,4-Dioxane, ethanol, N,N-dimethylformamide (DMF), and isopropanol were purchased from Tianjin Concord Technology Co., Ltd. (Tianjin, China). 1,3,5-triacetylbenzene (TAB), terephthalaldehyde (TPA) and 4,4'-biphenyldicarbaldehyde (BPDA) were purchased from Bide Pharmatech Ltd. (Shanghai, China). All reagents were analytically pure.

1.2. Instruments

Fourier transform infrared (FT-IR) spectra were obtained on TENSOR II (Bruker) spectrometer in wavenumber ranging from 4000 – 400 cm^{-1} . Solid ^{13}C -NMR experiments were performed on a Bruker AVANCE NEO 400 MHz wide-bore (89 mm) spectrometer. Scanning electron microscopy (SEM) characterization was carried out on a Shimadzu SS-550 scanning electron microscope. Thermogravimetric analysis (TGA) was performed on a Rigaku standard TG-DTA analyzer with a heating rate of 10 $^{\circ}\text{C}$ per minute in the range of ambient temperature to 850 $^{\circ}\text{C}$. Powder X-ray diffraction (PXRD) spectra were measured on A Rigaku SmartLab 9Kw system. Nitrogen adsorption/desorption isotherms were measured at 77 K on an ASAP 2460 instrument to obtain Brunauer–Emmett–Teller (BET) surface area. Photoluminescence spectra were recorded on a RF-5301-PC spectrophotometer. Fluorescence lifetime and quantum yield in DMF were measured on a FLS920 spectrophotometer. Solid-state photoluminescence spectra and quantum yield were recorded on a QM/TM/NIR spectrophotometer. Electrospun nanofiber films were obtained from the Nanospider NS LAB (ELMARCO, Czech Republic).

2 Synthesis of COPs using TAB and TPA

Both single and dual-color COPs were synthesized using alkali (*e.g.*, NaOH)-catalyzed aldol condensation reaction (Scheme S1). Single-color COPs were obtained under dilute alkali condition, and dual-color COPs were prepared under concentrated alkali condition (Scheme 1, main text).



Scheme S1. Mechanism of alkali-catalyzed aldol condensation reaction.

2.1 Synthesis of $\text{COP}_{\text{TAB-TPA}}$ (DC)

1,3,5-triacetylbenzene (TAB, 0.6 mmol) and terephthalaldehyde (TPA, 0.6 mmol) were dissolved in 12 mL ethanol and sonicated for 10 minutes. After addition of 0.6 mL NaOH (6 M), the mixture was transferred to a reactor with polytetrafluoroethylene lining. Then, the mixture was incubated at 120 °C for 3 days to prepare $\text{COP}_{\text{TAB-TPA}}$ (DC). The resultant product was isolated by centrifugation and washed with water (3×50 mL), DMF (3×50 mL), 1,4-dioxane (3×50 mL) and ethanol (3×50 mL) for three times. Finally, the obtained product was dried in vacuum at 70 °C to afford orange $\text{COP}_{\text{TAB-TPA}}$ (DC) powders with a yield of 87%.

2.2 Synthesis of COP_{TAB-TPA}(SC)

COP_{TAB-TPA}(SC) was prepared by the same procedures as above except that 0.1 mL NaOH (6 M) was added. The yellow COP_{TAB-TPA}(SC) was obtained with a yield of 67%.

2.3 Synthesis of fluorescent COPs under different conditions

We investigated the reaction conditions in detail (Table S1). The reaction temperature was changed from room temperature to 120 °C, and the reaction time was varied from 6 to 72 h. When the amount of catalyst (6 M NaOH) is more than 0.3 mL, COP_{TAB-TPA}(DC) with dual-color emission can be obtained, and orange fluorescence can be observed by the naked eyes (Figure S1). When the amount of catalyst is below 0.1 mL, COP_{TAB-TPA}(SC) with single-color emission can be obtained with no obvious fluorescence observed by the naked eyes (Figure S1).

Table S1 Synthesis of COPs under different conditions

	Solvent	NaOH (6M)	Temperature	Time	emission	Yield
1	Ethanol	0.6 mL	120 °C	72 h	Dual-color	87%
2	Ethanol	0.6 mL	120 °C	6 h	Dual-color	86%
3	Ethanol	0.6 mL	120 °C	12 h	Dual-color	79%
4	Ethanol	0.6 mL	120 °C	18 h	Dual-color	92%
5	Ethanol	0.6 mL	100 °C	18 h	Dual-color	84%
6	Ethanol	0.6 mL	80 °C	18 h	Dual-color (weak)	74%
7	Ethanol	0.6 mL	60 °C	18 h	Dual-color (weak)	47%
8	Ethanol	0.6 mL	Room temperature	72 h	Dual-color (weak)	51%
9	Ethanol	0.1 mL	120 °C	72 h	Single-color	67%
10	Ethanol	0.1 mL	120 °C	18 h	Single-color	60%
11	Ethanol	0.1 mL	120 °C	18 h	Dual-color	85%
12	Ethanol	1.2 mL	120 °C	72 h	Dual-color	68%
13	Ethanol	2.4 mL	120 °C	72 h	Dual-color	62%
14	1,4-dioxane	1.2 mL	120 °C	72 h	Dual-color (weak)	65%
15	1,4-dioxane	0.6 mL	120 °C	72 h	Dual-color (weak)	68%
16	1,4-dioxane	0.6 mL	Room temperature	72 h	Dual-color (weak)	63%
17	1,4-dioxane/ethanol (1:1)	0.1 mL	120 °C	72h	Single-color	95%
18	1,4-dioxane/ethanol (1:1)	0.3 mL	120 °C	72h	Dual-color	98%
19	1,4-dioxane/ethanol (1:1)	0.6 mL	120 °C	72h	Dual-color	97%
20	1,4-dioxane/ethanol (1:1)	1.2 mL	120 °C	72h	Dual-color	99%

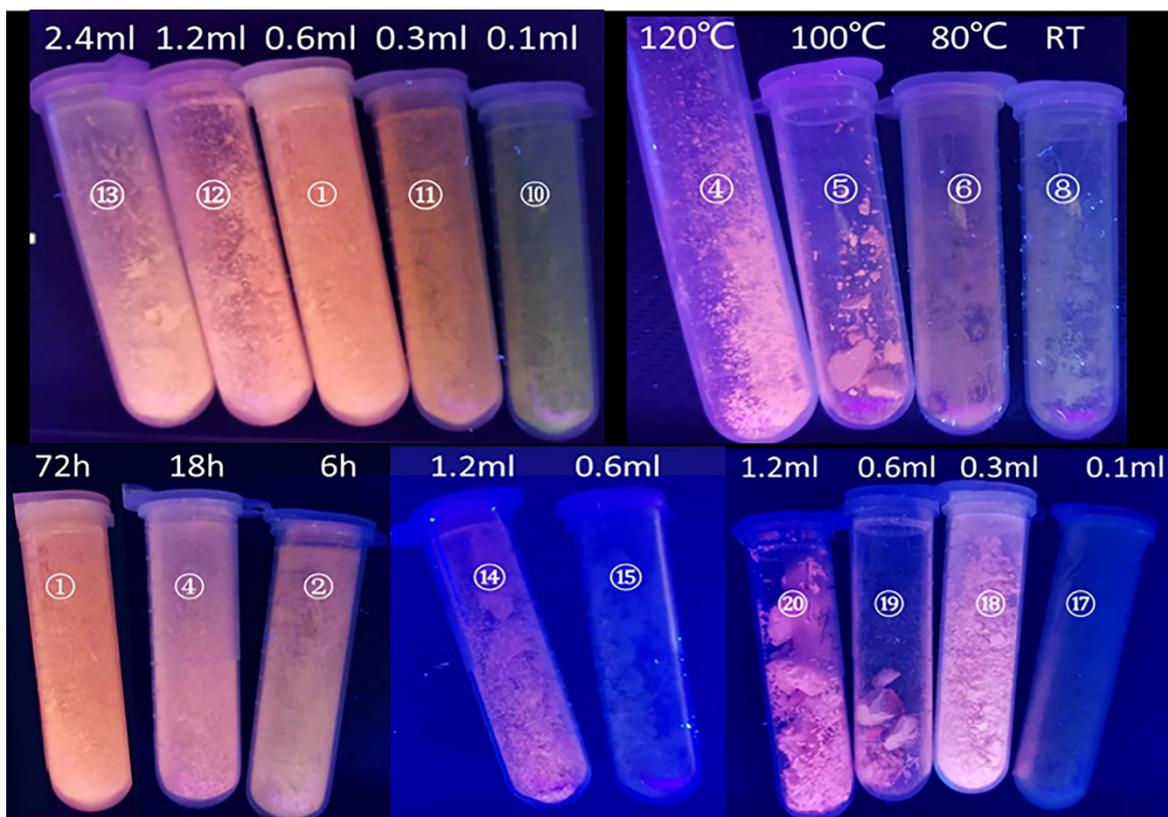
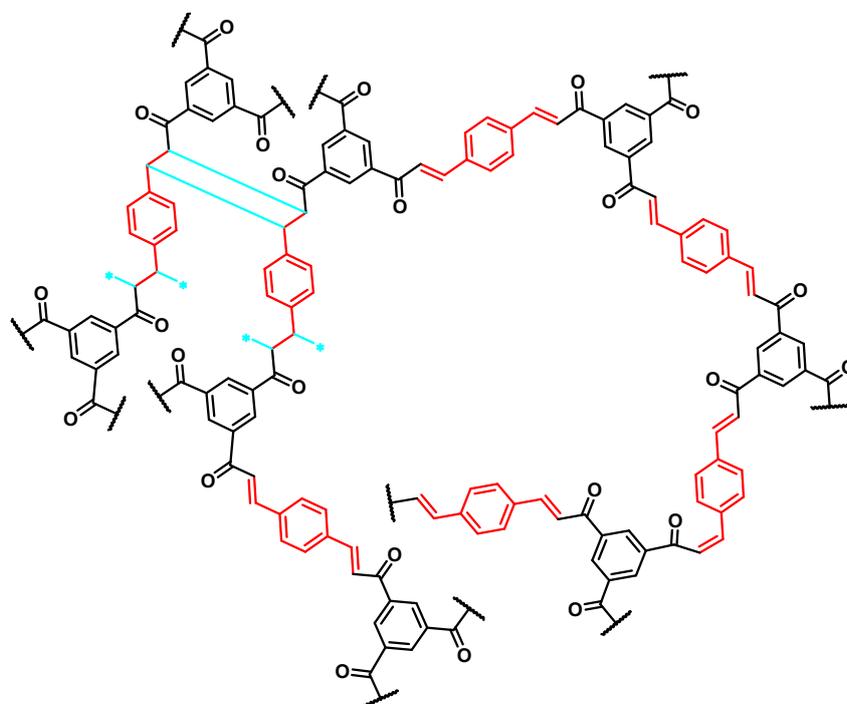


Figure S1. Images of COPs obtained under different reaction conditions (ultraviolet light excitation).

3. Schematic diagram of the addition polymerization reaction of C=C



Scheme S2. Schematic diagram of the addition polymerization reaction of C=C to form cyclobutane in COPs, taking COP_{TAB-TPA(SC)} as an example.

Results and Discussion

1. Thermogravimetric analysis of COPs

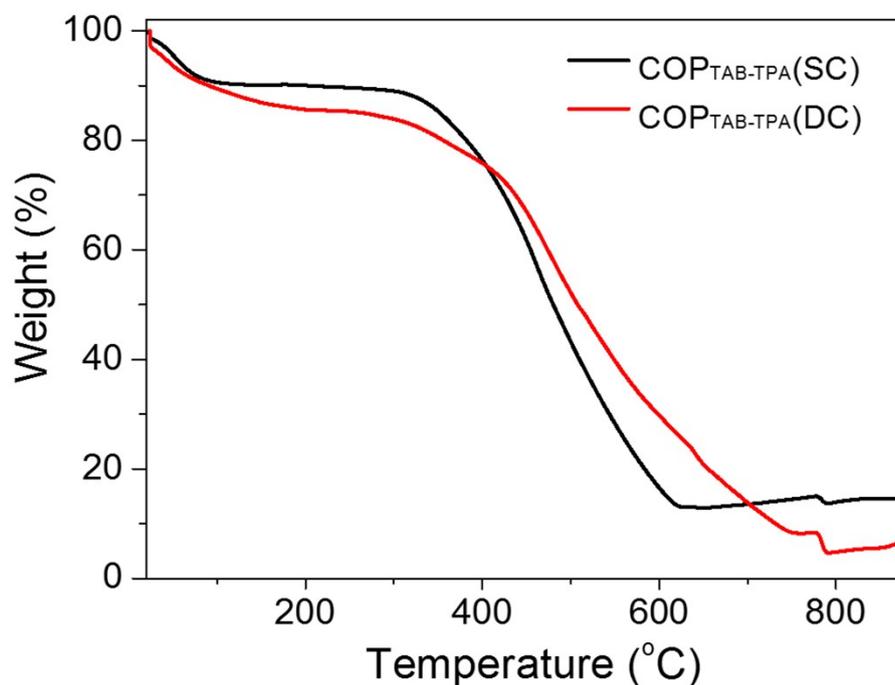


Figure S2. Thermogravimetric analysis of COP_{TAB-TPA}(SC) and COP_{TAB-TPA}(DC)

2. Chemical stability of COPs

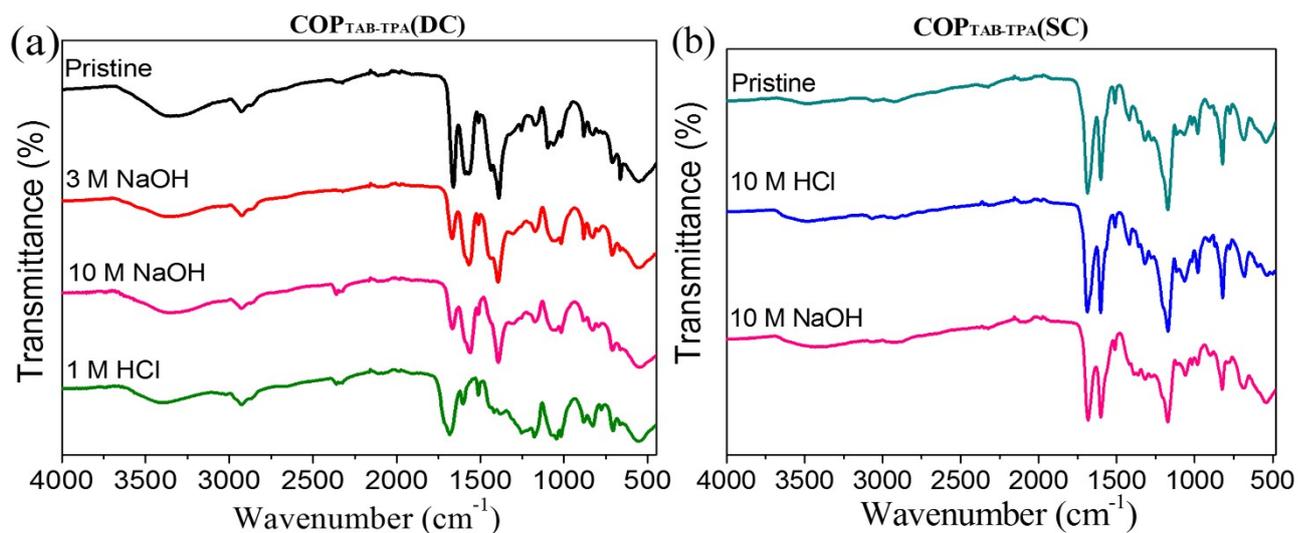


Figure S3. FT-IR spectra of (a) COP_{TAB-TPA}(DC) and (b) COP_{TAB-TPA}(SC) before and after acid or alkali treatment.

3. Powder X-ray diffraction characterization of COP_{TAB-TPA}(DC)

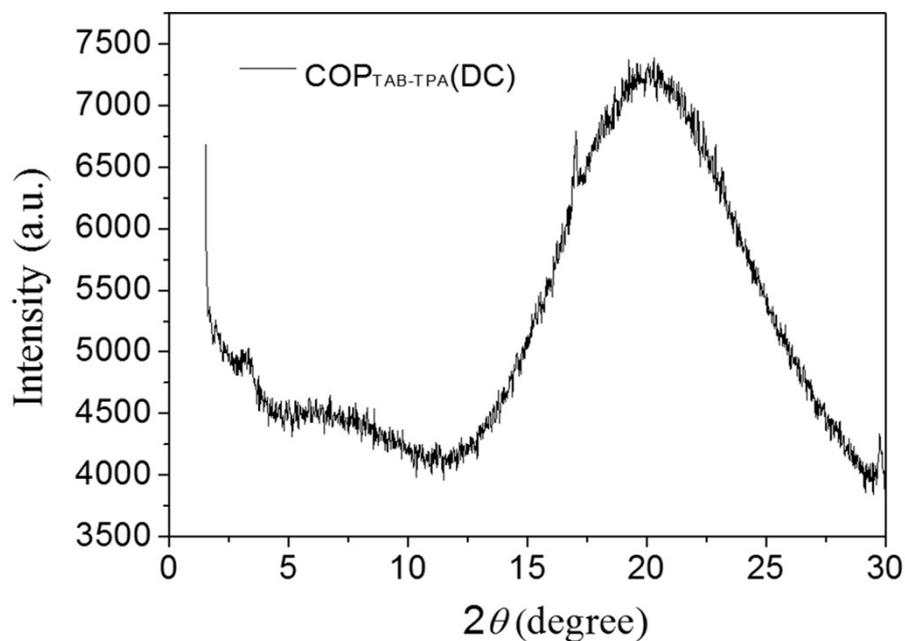


Figure S4. The powder X-ray diffraction pattern of COP_{TAB-TPA}(DC)

4. N₂ adsorption-desorption measurement of COP_{TAB-TPA}(DC)

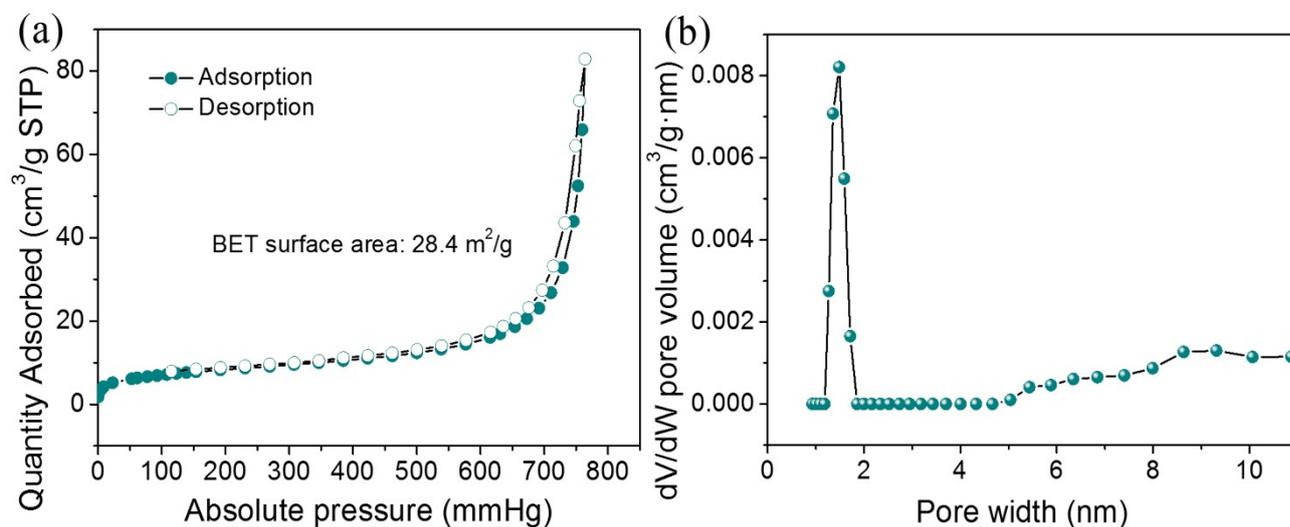


Figure S5. (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of COP_{TAB-TPA}(DC).

5. Excitation and emission spectra of COP_{TAB-TPA}(SC) in DMF

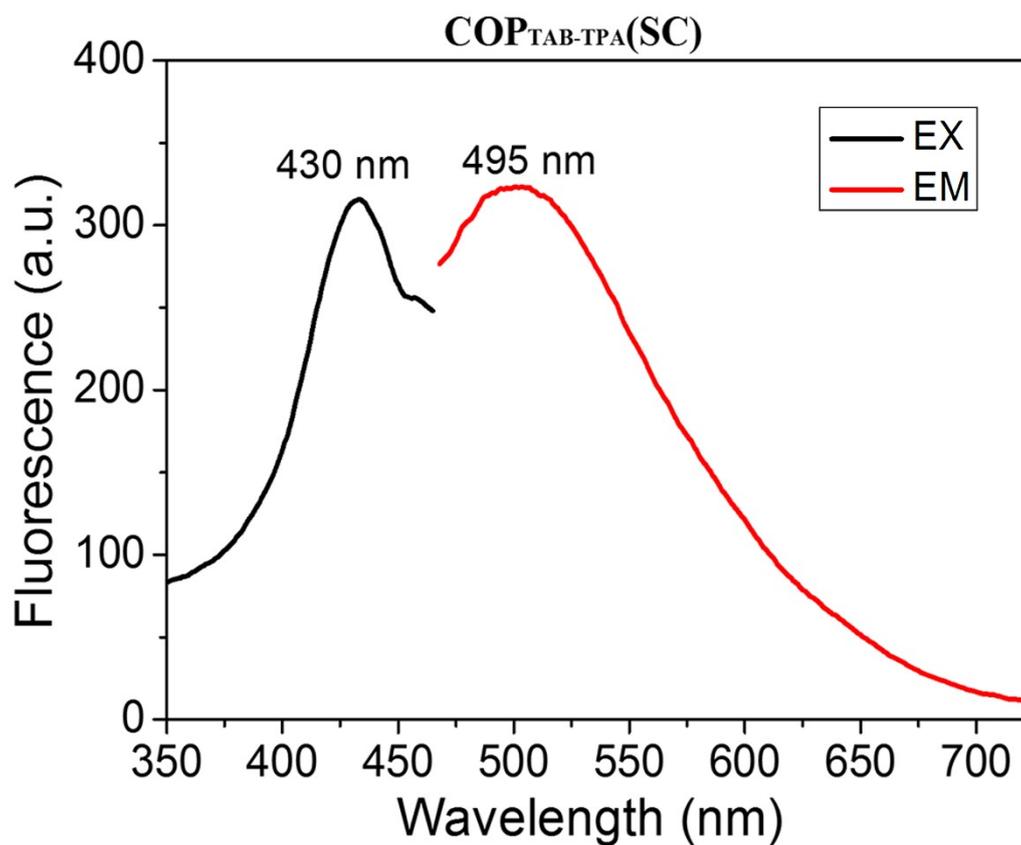


Figure S6. Excitation and emission spectra of COP_{TAB-TPA}(SC) in DMF.

6. Excitation and emission spectra of COP_{TAB-TPA}(DC) in DMF

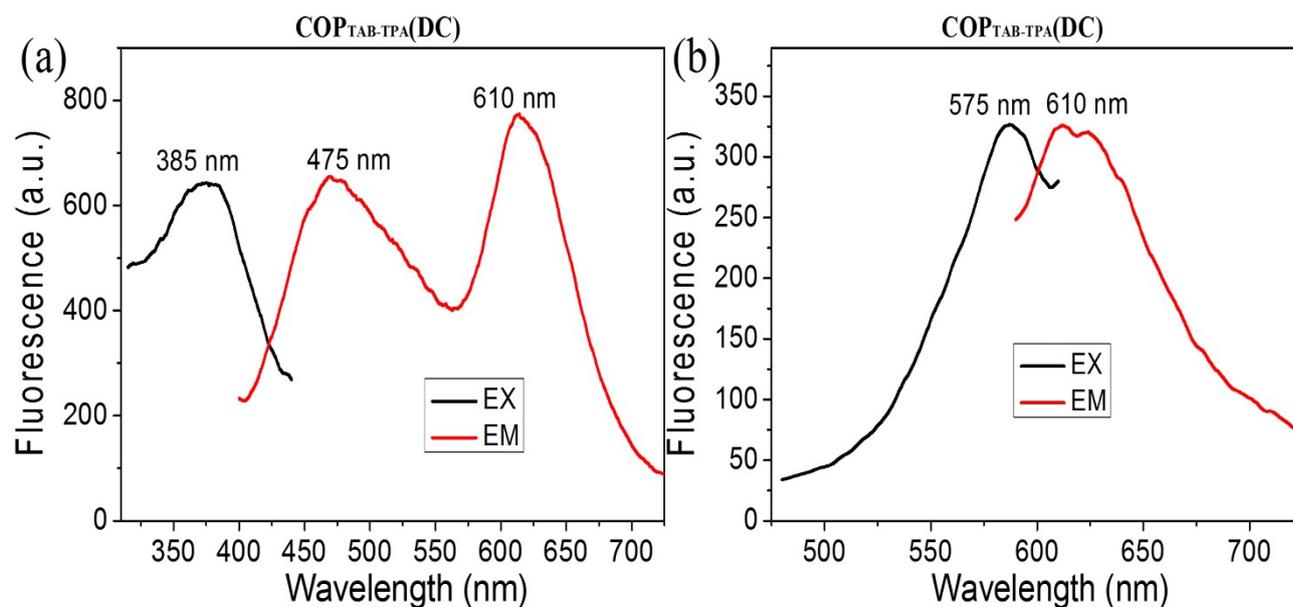


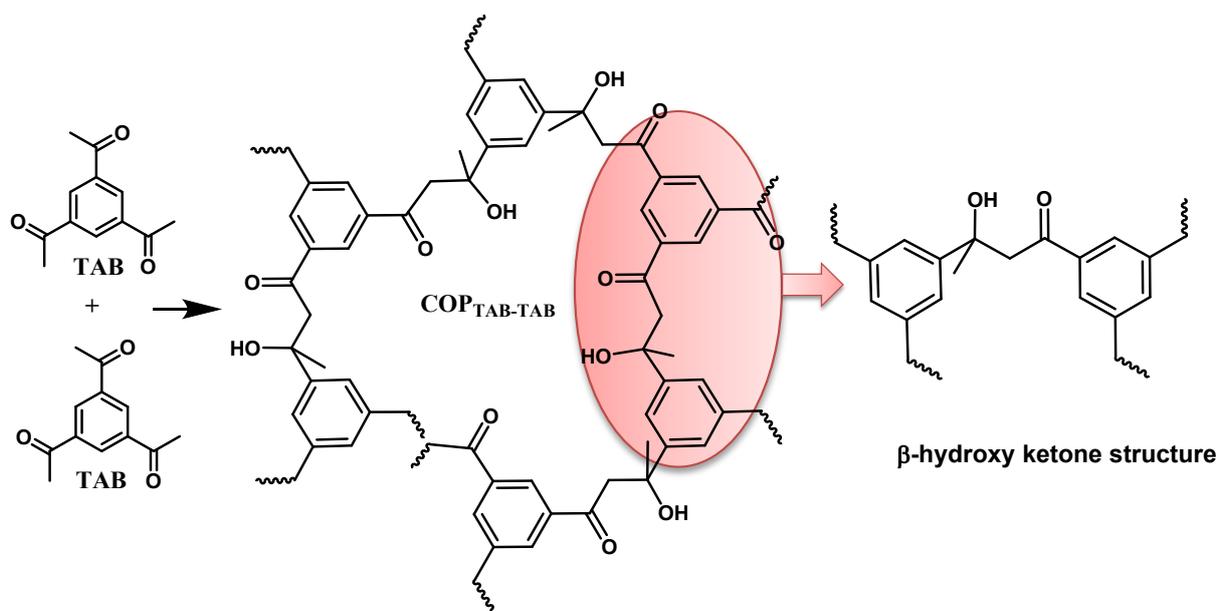
Figure S7. Excitation and emission spectra of COP_{TAB-TPA}(DC) in DMF. 385 nm and 575 nm are used as the excitation wavelength in (a) and (b), respectively. The excitation spectrum in (a) is recorded by using 475 nm as the emission wavelength.

7. Preparation and characterization of COP_{TAB-TAB}

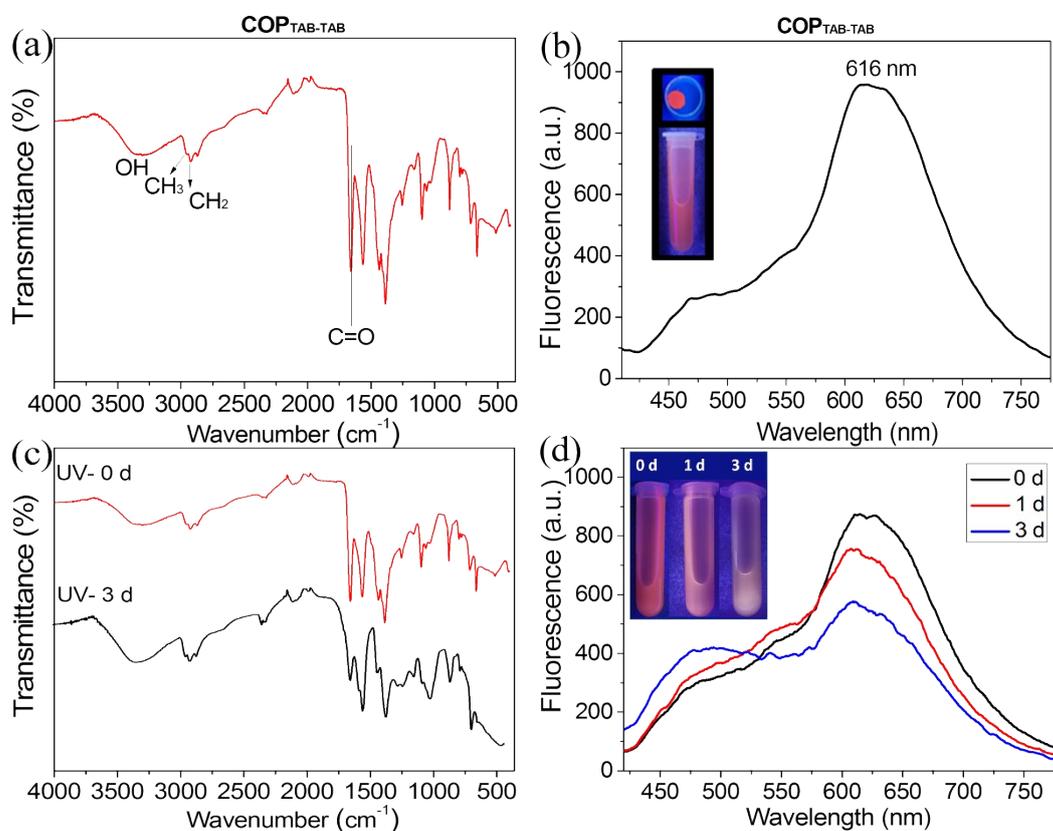
7.1 Preparation of COP_{TAB-TAB} by the self-condensation of TAB

Self-condensation reaction 1,3,5-triacetylbenzene (TAB) was carried out to prepare COP_{TAB-TAB} (Scheme S3). Briefly, TAB (0.3 mmol) was dissolved in ethanol (3 mL) and sonicated for 10 minutes. After addition of 0.1 mL NaOH (6 M), the mixture was transferred to a reactor with polytetrafluoroethylene lining. Then, the mixture was incubated at 120 °C for 3 days to prepare COP_{TAB-TAB}. The resultant product was isolated by centrifugation and washed with water (3 × 50 mL), DMF (3 × 50 mL), 1,4-dioxane (3 × 50 mL) and ethanol (3 × 50 mL) for three times. Finally, the obtained product was dried in vacuum at 70 °C to afford red COP_{TAB-TAB} powders with a yield of 48%.

Due to the low reactivity of the carbonyl group in TAB and the large steric hindrance of the reaction product, the reaction balance of TAB self-condensation tends to form β-hydroxy ketone (HO–C–C–C=O) structure. The FT-IR spectrum of COP_{TAB-TAB} shows the characteristic peaks of –OH at 3306 cm⁻¹, –CH₃ at 2952 cm⁻¹ and –CH₂– at 2925 cm⁻¹, and almost no C=C signal is observed around 1600 cm⁻¹ (Figure S8a), confirming the β-hydroxy ketone (HO–C–C–C=O) structure in COP_{TAB-TAB}. The fluorescence spectrum of COP_{TAB-TAB} shows a strong fluorescence emission at 616 nm, and bright red fluorescence is observed by the naked eyes (Figure S8b), which gives a strong evidence that the emission at 610 nm of COP_{TAB-TPA} (DC) is attributed to the β-hydroxy ketone (HO–C–C–C=O) structure.



7.2 Characterization of $\text{COP}_{\text{TAB-TAB}}$



The infrared spectrum of COP_{TAB-TAB} did not change significantly. The emission spectrum at 616 nm experienced a common photobleaching, and the intensity was significantly reduced, while a slightly enhancement at 490 nm may be attributed to the inevitable presence of a small amount of dehydration structure (allyl ketone; C=C-C=O) in COP_{TAB-TAB}, which can undergo a [2+2] cycloaddition under UV irradiation to increase the fluorescence. And the color of COP_{TAB-TAB} changes from red to dark yellow.

8. FT-IR spectra of COP_{TAB-TPA(DC)} before and after UV irradiation

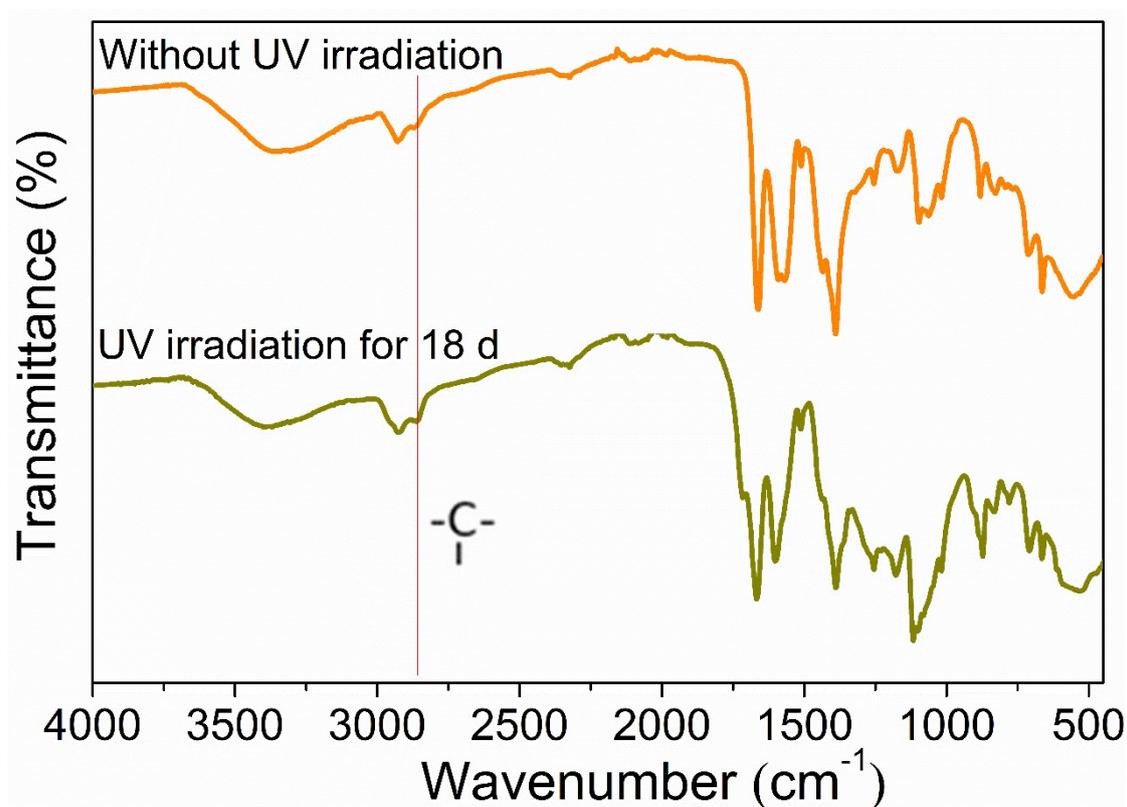


Figure S9. FT-IR spectra of COP_{TAB-TPA(DC)} before and after UV irradiation for 18 d. The methine vibration signal at 2873 cm⁻¹ is enhanced, indicating the formation of cyclobutane.

9. ^{13}C -NMR of chalcone molecule before and after UV irradiation

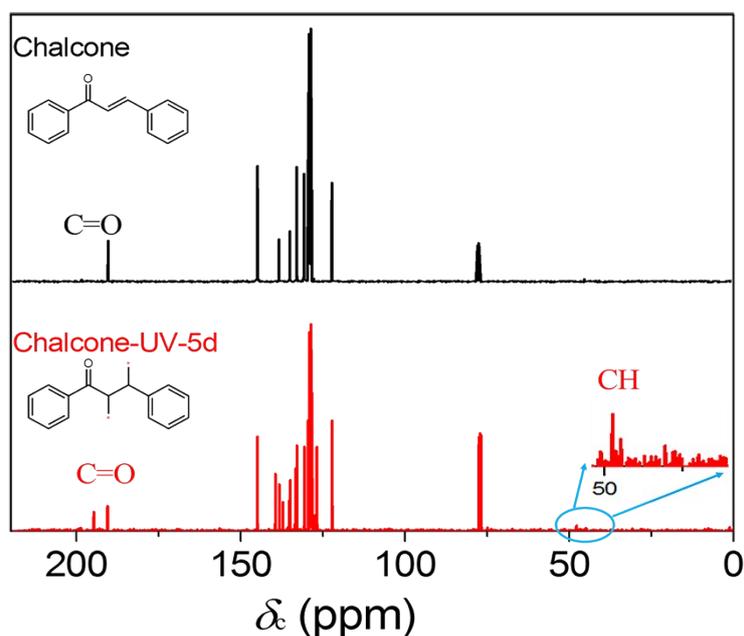


Figure S10. The liquid ^{13}C -NMR of chalcone molecule before and after UV irradiation for 5 d.

We selected the allyl ketone type representative, chalcone molecule, for further verification. From its liquid ^{13}C -NMR, the C-H peak appears after UV irradiation for 5 days, and a new C=O peak at a lower field appeared, which was attributed to the decrease of conjugation after the cycloaddition, indicating the progress of the [2+2] cycloaddition reaction.

10. $\text{COP}_{\text{TAB-TPA}}(\text{DC})$ prepared in 1,4-dioxane/ethanol-mixed solvent

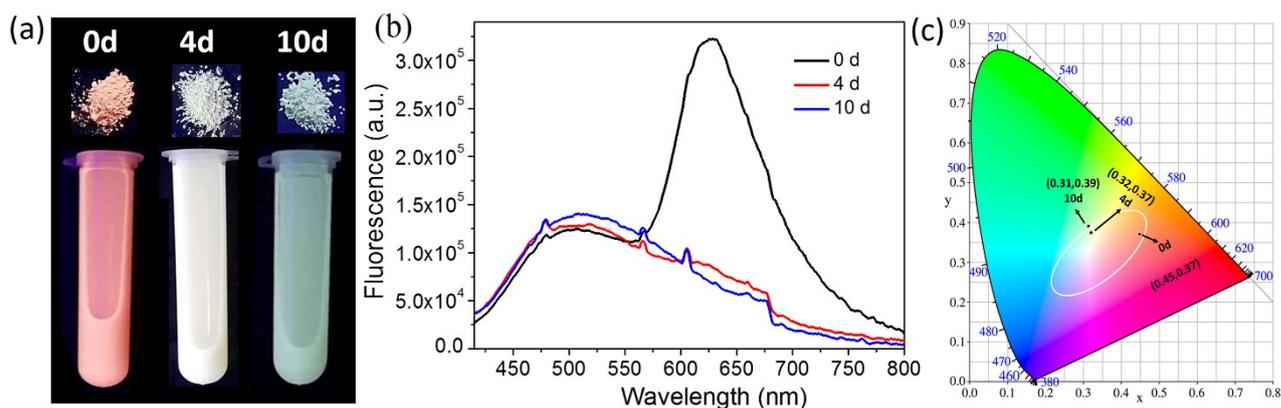


Figure S11. Changes of (a) luminous color in DMF and in solid state, (b) solid state fluorescence spectrum, and (c) CIE coordinate of $\text{COP}_{\text{TAB-TPA}}(\text{DC})$ prepared in 1,4-dioxane/ethanol-mixed solvent after treatment with UV irradiation for different time. In (b), the excitation wavelength is 390 nm.

11. Reversibility of color transition of COP_{TAB-TPA}(DC)

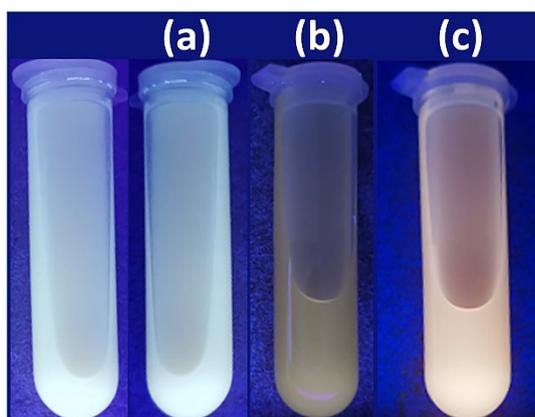


Figure S12. (a) Natural light treatment for 7 d, (b) Heating at 200 °C for 10 h (c) under its reaction conditions (ethanol 12 mL, NaOH-6 M-0.6 mL, 120 °C, 2 h)

The white fluorescent COP solid was placed under natural light for 7 days, and there was no obvious change in (a). Then we tried to heat the white fluorescent COP solid at 200 °C for 10 hours, which is a reverse cycloaddition reaction conditions reported by Jadhav et al. ¹ in 2020. The COP changed from white to khaki, indicating that high temperature may be the condition for the reversible color change, but the luminous intensity is obviously dimmed in (b). Next, we tried to treat the white fluorescent COP under its synthesis conditions (ethanol 12 mL, NaOH - 6 M - 0.6 mL, 120 °C, 2 h), the color change showed a certain degree of reversible transformation in (c). We speculated that the structure was reshaped under the reaction conditions, and the structure torsion and damage caused by photobleaching was restored.

12. Emission curves of natural light and artificial light

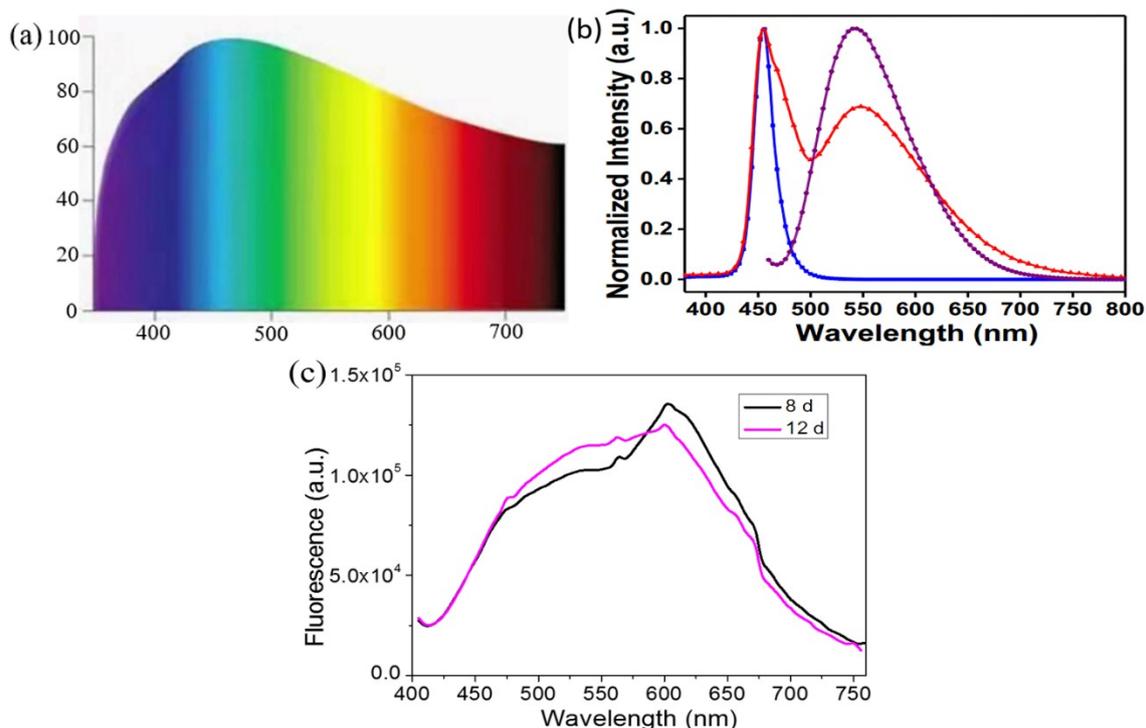


Figure S13. (a) Spectral curve of natural light. (b) Spectral curves of artificial lights reported by Yang et al.² and Ding et al.³ Their emission spectra are discontinuous and lack red light. (c) Spectral curves of COP_{TAB-TPA}(DC) after UV irradiation treatment for 8 d and 12 d. Their emission spectra are more close to the natural light spectral curve, and the CCTs are calculated to 3857 K and 4461 K, respectively, both within the color temperature range of natural white light.

13. The luminous life of the WLED



Figure S14. The change of WLED working continuously for 10 days

During the continuous working period, the WLED gradually changed from warm white to bright white in the first 3 days. After 7 days, blue-violet light leakage appears faintly, and some materials are inactivated by photobleaching. After 10 days, blue-violet light can be clearly seen, and the material that loses fluorescence is further increased. Therefore, the fluorescent life of this WLED is within 7 days.

14. Electrospun nanofiber films

Number	COP _{TAB-TPA} (DC)		Mass ratio of COP _{TAB-TPA} (DC) to PAN	CIE coordinate of film
	Time for UV irradiation	CIE coordinate		
1			0:1	(0.27, 0.24)
2	8 d	(0.39, 0.39)	1:40	(0.29, 0.33)
3	3 d	(0.41, 0.39)	1:40	(0.31, 0.32)
4	0 d	(0.48, 0.37)	1.5:100	(0.31, 0.31)

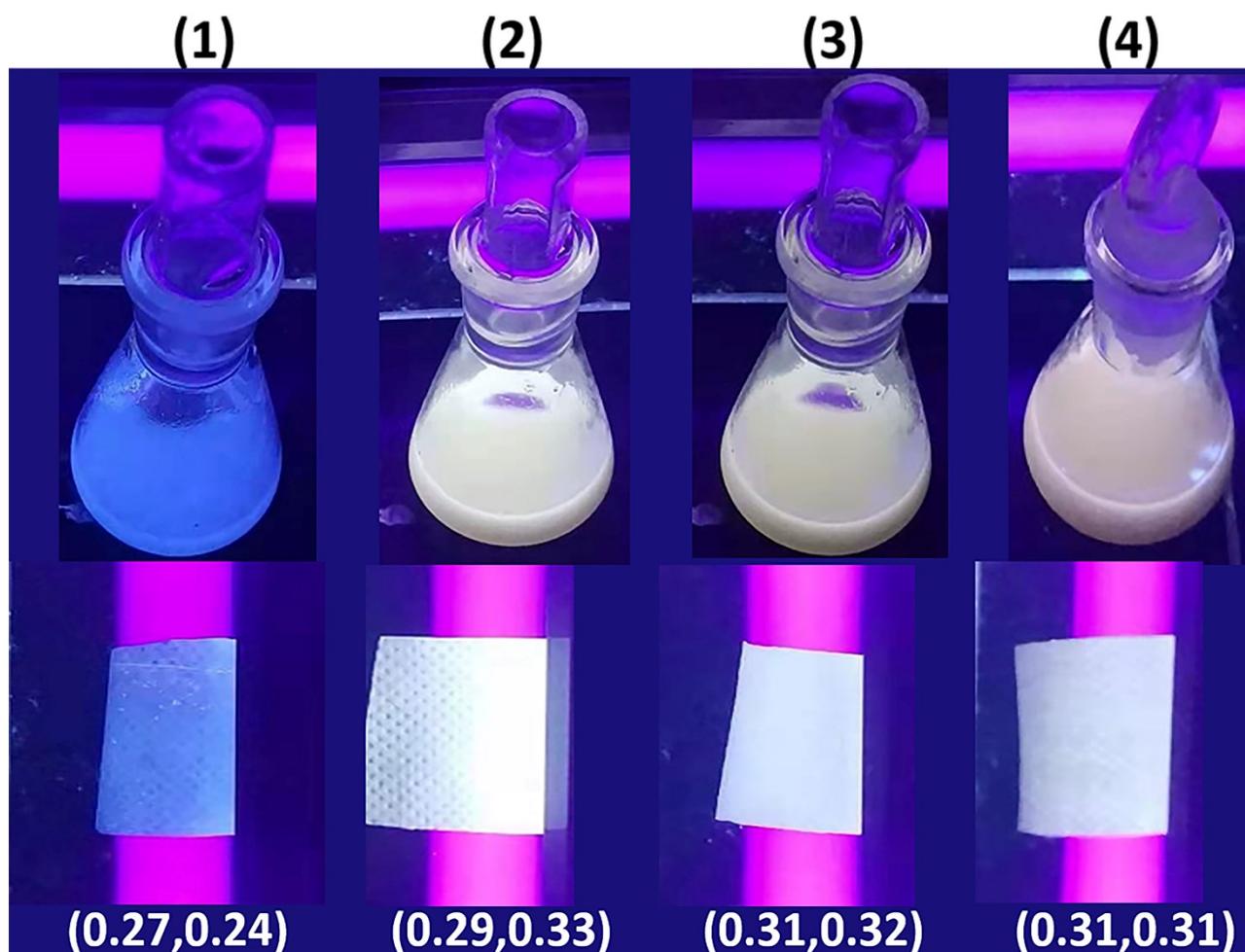


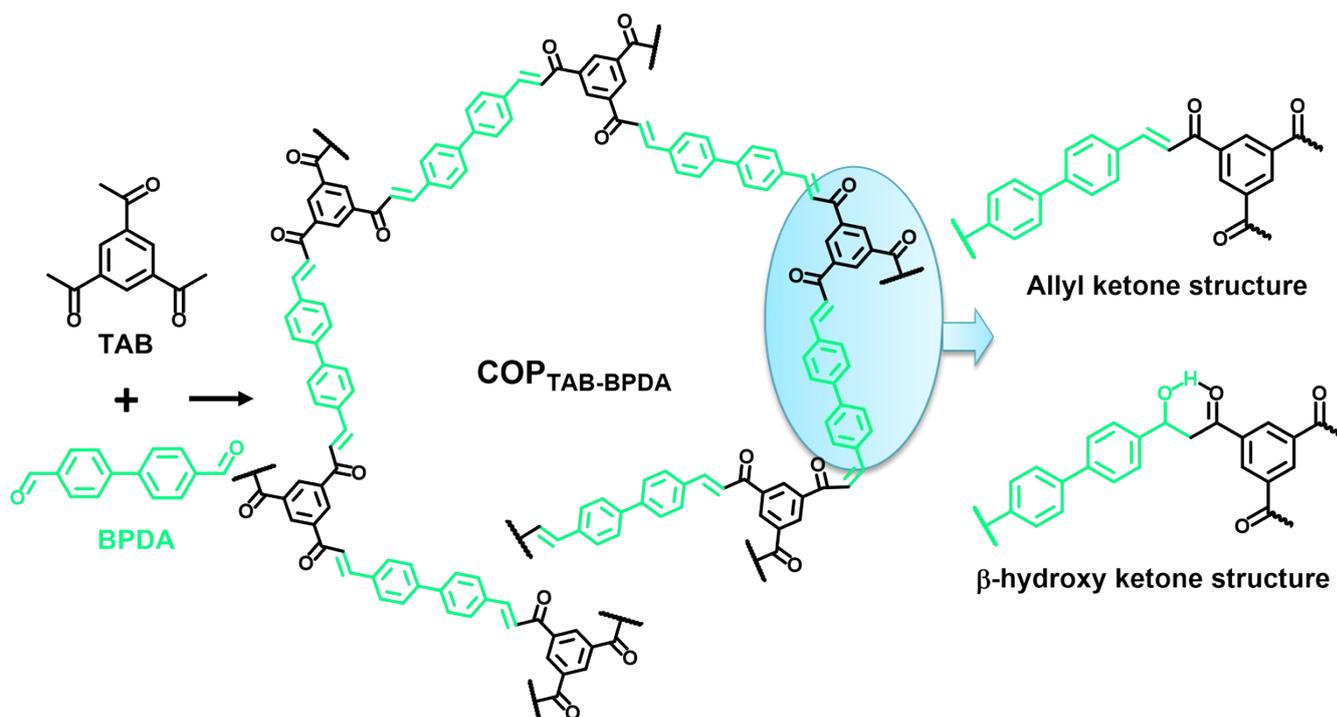
Figure S15. Flexible white light films prepared by electrospinning and their applications in WLEDs. The table shows the used COP_{TAB-TPA(DC)}, mass ratio of COP_{TAB-TPA(DC)} to PAN, and the CIE coordinates of the prepared films.

15. Synthesis of COPs using TAB and BPDA

15.1 Synthesis of COP_{TAB-BPDA (DC)}

Dual-color COP_{TAB-BPDA (DC)} and COP_{TAB-BPDA (SC)} were also synthesized by alkali-catalyzed aldol condensation reaction, and obtained under concentrated and dilute alkali conditions, respectively (Scheme S4). For the preparation of COP_{TAB-BPDA (DC)}, 1,3,5-triacetylbenzene (TAB, 0.6 mmol) and 4,4'-biphenyldicarbaldehyde (BPDA, 0.6 mmol) were dissolved in 12 mL ethanol and sonicated for 10 minutes. After addition of 0.3 mL NaOH (6 M), the mixture

was transferred to a reactor with polytetrafluoroethylene lining. Then, the mixture was incubated at 120 °C for 3 days to prepare COP_{TAB-BPDA}(DC). The resultant product was isolated by centrifugation and washed with water (3 × 50 mL), DMF (3 × 50 mL), 1,4-dioxane (3 × 50 mL) and ethanol (3 × 50 mL) for three times. Finally, the obtained product was dried in vacuum at 70 °C to afford orange COP_{TAB-BPDA}(DC) powders with a yield of 94%.



Scheme S4. Preparation of COP_{TAB-BPDA}(SC) with only allyl ketone structure (C=C-C=O) and COP_{TAB-BPDA}(DC) with both allyl ketone (C=C-C=O) and β-hydroxy ketone (OH-C-C-C=O) structures.

15.2 Synthesis of COP_{TAB-BPDA} (SC)

COP_{TAB-BPDA}(SC) was prepared by the same procedures as above except that 0.05 mL NaOH (6 M) was added. The yellow-green COP_{TAB-BPDA}(SC) was obtained with a yield of 65%.

References

1. T. Jadhav, Y. Fang, C. H. Liu, A. Dadvand, E. Hamzehpoor, W. Patterson, A. Jonderian, R. S. Stein and D. F. Perepichka, *J. Am. Chem. Soc.*, 2020, **142**, 8862–8870.
2. M. J. Yang, C. S. Mo, L. Fang, J. Li, Z. K. Yuan, Z. Y. Chen, Q. C. Jiang, X. D. Chen and D. S. Yu, *Adv. Funct. Mater.*, 2020, **30**, 2000516.
3. H. M. Ding, J. Li, G. H. Xie, G. Q. Lin, R. F. Chen, Z. K. Peng, C. L. Yang, B. S. Wang, J. L. Sun and C. Wang, *Nat. Commun.*, 2018, **9**, 5234.