

Supporting information

Flexible Organic Crystals with Multi-Stimuli-Responsive CPL for Broadband Multicolor Optical Waveguides

General information

All chemicals for syntheses were purchased from commercial sources. The solvents for syntheses were analytical-reagent grade and were used without further purification. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured on a Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. UV–vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The CD spectra were recorded with PMS 450 spectrometer. The CPL spectra were recorded with JASCO CPL-300 spectrometer. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer or a Maya2000 Pro CCD spectrometer. The crystal slice was irradiated by the third harmonic (355 nm) of a Nd: YAG (yttrium-aluminum-garnet) laser with a pulse duration of about 5 ns. The energy of laser was adjusted by using the calibrated neutral density filters. The beam was focused into a stripe whose shape was adjusted to 3.3×0.6 mm by using a cylindrical lens and a slit. The emission was detected at one end of the crystal using a Maya2000 Pro CCD spectrometer. Three-point bending tests were carried out on the N. 5944 universal materials tester produced by Instron Corporation. The single-crystal X-ray diffraction data were collected on a Rigaku Synergy-DS Diffractometer. The structures were solved with direct methods using the Olex2 program and refined with full-matrix least-squares on F2.^[1] The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated and refined isotropically. The crystallographic information has been deposited at the Cambridge Crystallographic Data Centre (CCDC). The CCDC deposition number for *S*-**1** is 2373506 and for *R*-**1** is 2373505.

Crystal growth method: The nearly saturated dichloromethane (analytically pure) solution of compound **1** (0.3 M in CH_2Cl_2 , 30 mL) was added to a 100 mL beaker and then 1.5 times the volume of cyclohexane was carefully added along the inner wall of the beaker while ensuring that the two phases remained separated. The beaker was sealed with parafilm and left standing at room temperature for about 7–10 days, yielding a large number of yellow needle-shaped crystals (up to centimeters long, tens to hundreds of micrometers thick, and hundreds of micrometers wide).

Theoretical calculation: Based on the experimentally measured single-crystal X-ray diffraction structure of *S*-**1**, we constructed the enol, *cis*-keto, and *trans*-keto configurations. The HOMO, LUMO of the enol form were calculated at the B3LYP/6-31G (d, p) level using Gaussian 09 software, with Grimme's D3 version of dispersion correction applied. The IR spectra of the enol, *cis*-keto, and *trans*-keto forms were calculated at the B3LYP/6-31G (d) level using Gaussian 09 software, with Grimme's D3 version of dispersion correction applied.

Supplementary figures

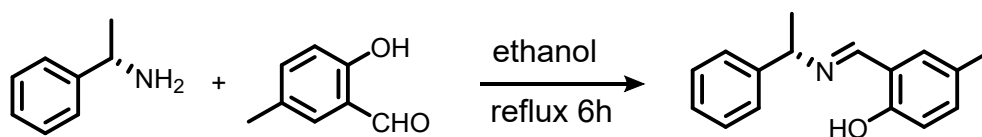


Figure S1. The synthetic procedure of *S*-1 compound.

S-1. (*S*)-1-phenyl-1-amine (1.20 g, 10 mmol) and 2-hydroxy-5-methylbenzaldehyde (1.36 g, 10 mmol) were heated in ethanol (40 mL) at 79 °C for 6 hours. After cooled to room temperature, the reaction mixture was filtered. The filter cake was dried and purified by column chromatography (silica gel, 2:1 petroleum ether/dichloromethane) to provide *S*-1 as a yellow solid (2.06 g, 80%). ¹H NMR (500 MHz, DMSO-*d*₆) δ = 13.20 (s, 1H), 8.62 (s, 1H), 7.34 – 7.42 (m, 4H), 7.23 – 7.32 (m, 2H), 7.15 (dd, *J*=2.3, 8.4, 1H), 6.79 (d, *J*=8.4, 1H), 4.65 (q, *J*=6.6, 1H), 2.24 (s, 3H), 1.54 (d, *J*=6.7, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ = 164.7, 158.6, 144.6, 133.5, 132.1, 129.1, 127.7, 127.6, 126.8, 118.9, 116.7, 67.5, 24.9, 20.4.

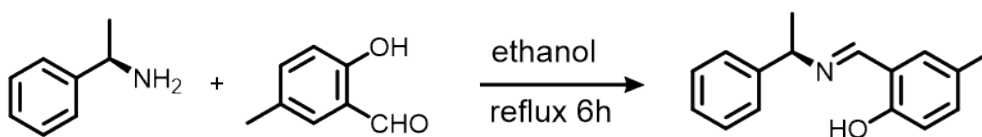


Figure S2. The synthetic procedure of *R*-1 compound.

R-1. (*R*)-1-phenyl-1-amine (1.20 g, 10 mmol) and 2-hydroxy-5-methylbenzaldehyde (1.36 g, 10 mmol) were heated in ethanol (40 mL) at 79°C for 6 hours. After cooled to room temperature, the reaction mixture was filtered. The filter cake was dried and purified by column chromatography (silica gel, 2:1 petroleum ether/dichloromethane) to provide *R*-1 as a yellow solid (2.01g, 78%). ¹H NMR (500 MHz, DMSO-*d*₆) δ = 13.20 (s, 1H), 8.63 (s, 1H), 7.34 – 7.43 (m, 4H), 7.23 – 7.33 (m, 2H), 7.15 (dd, *J*=2.3, 8.4, 1H), 6.79 (d, *J*=8.3, 1H), 4.65 (q, *J*=6.6, 1H), 2.24 (s, 3H), 1.55 (d, *J*=6.7, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ = 164.7, 158.6, 144.6, 133.5, 132.1, 129.1, 127.7, 127.6, 126.8, 118.9, 116.7, 67.5, 24.9, 20.4.

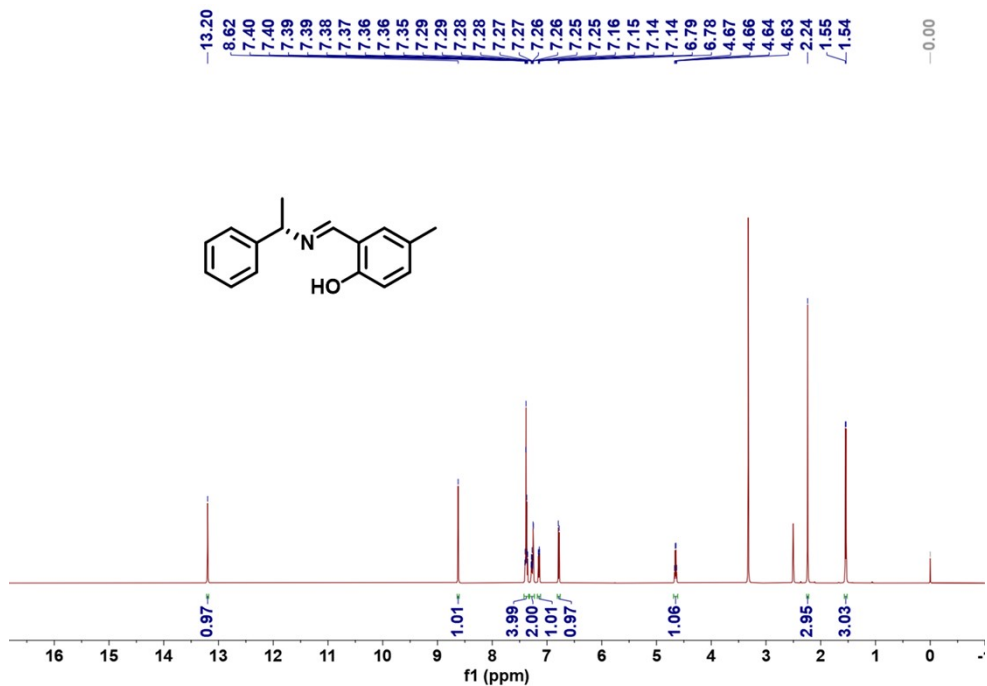


Figure S3. ¹H NMR spectrum of S-1 compound.

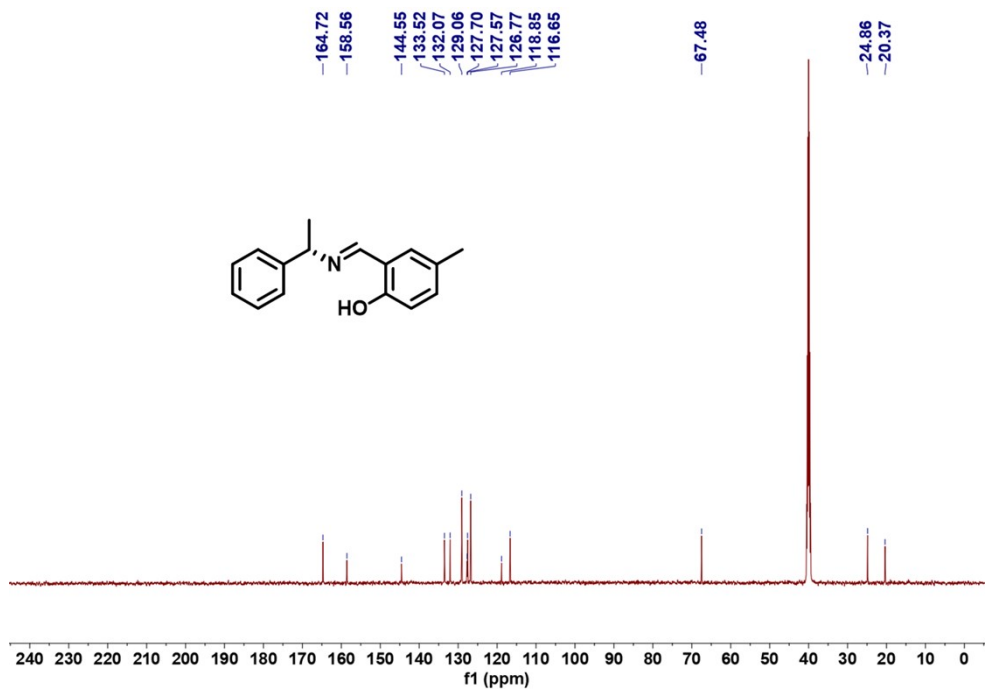


Figure S4. ¹³C {¹H} NMR spectrum of S-1 compound.

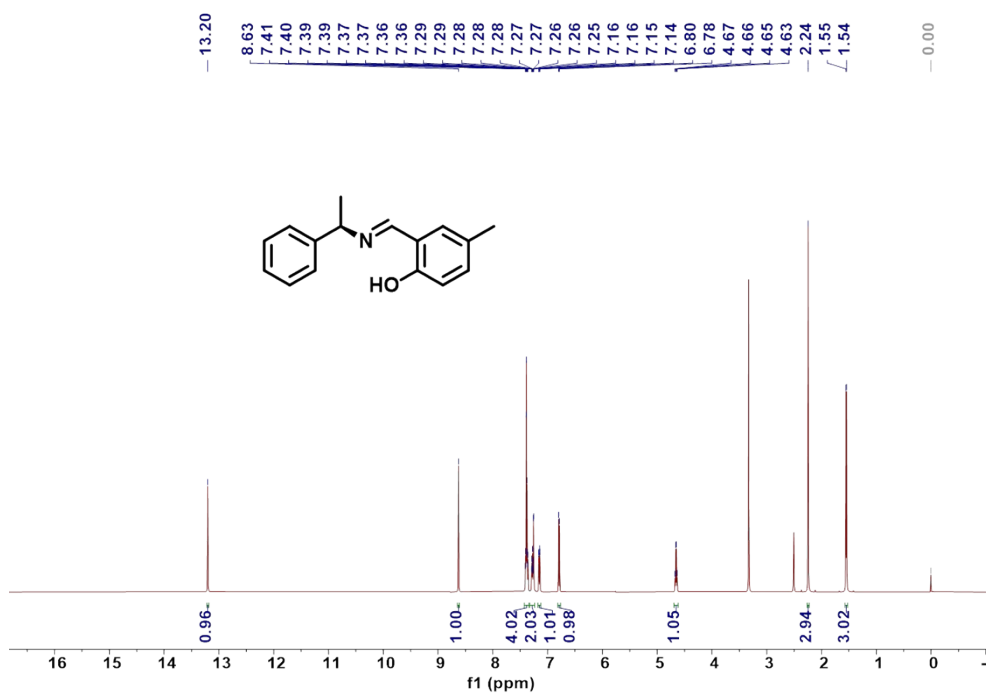


Figure S5. ^1H NMR spectrum of *R*-1 compound.

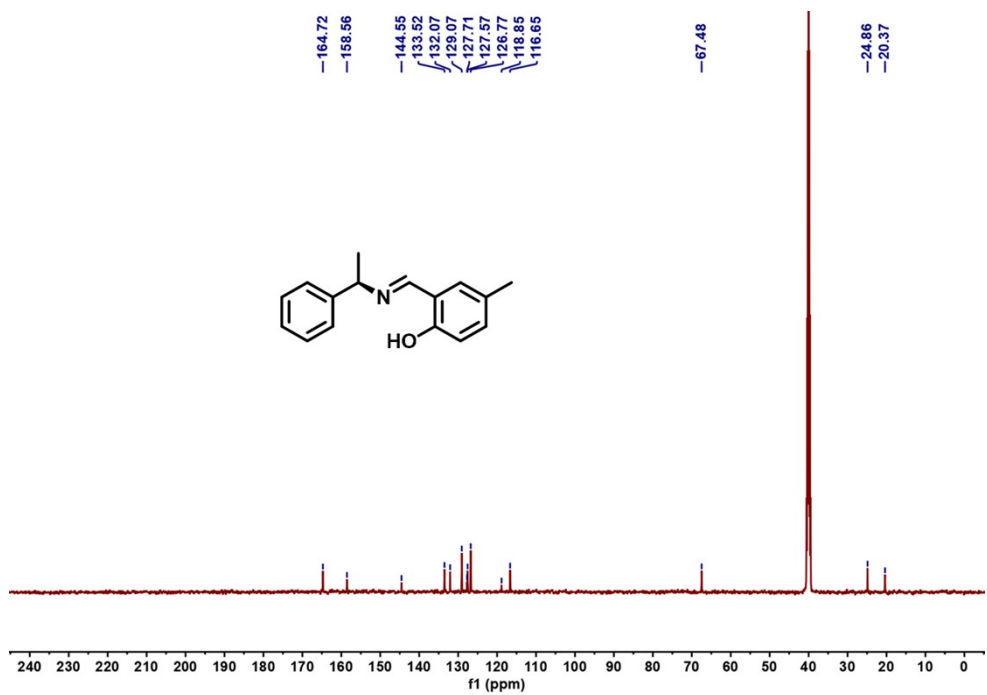


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *R*-1 compound.

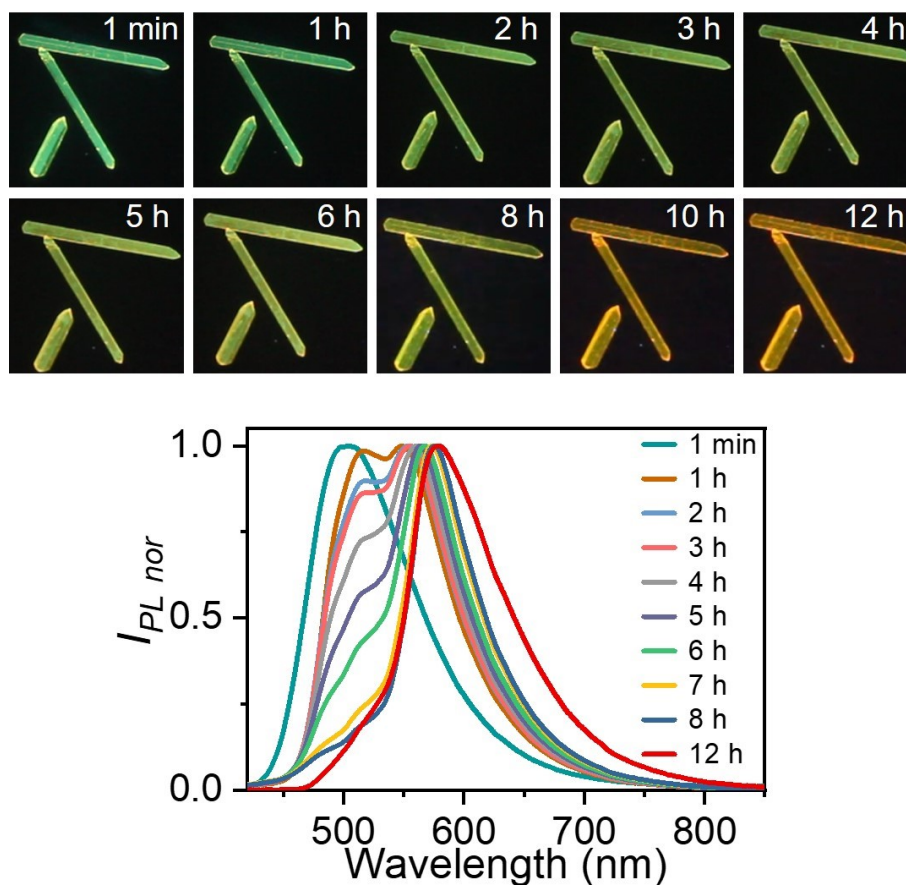


Figure S7. Photographic images of *S-1@H* and the recovering processes of the protonated crystals and emission spectra of time-dependent deprotonation of *S-1@H*.

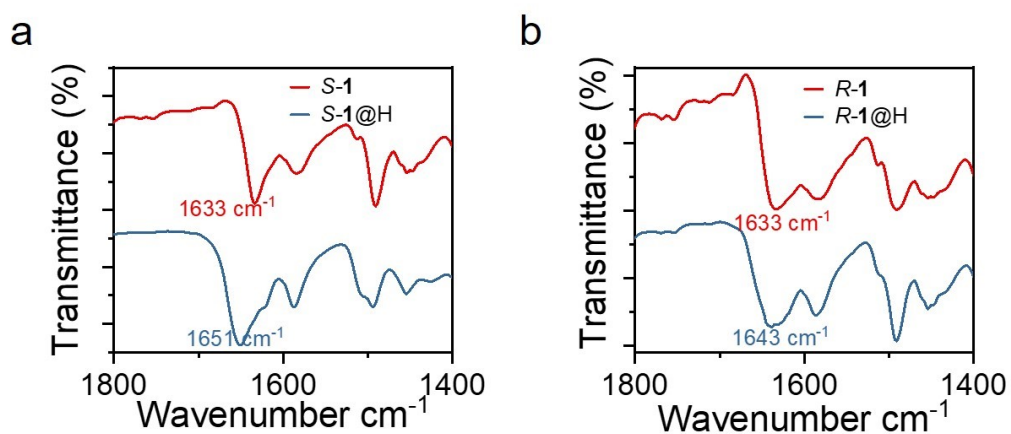


Figure S8. Experimental IR absorption spectra of *S-1* (a) and *R-1* (b) under original and hydrochloric acid fumigation.

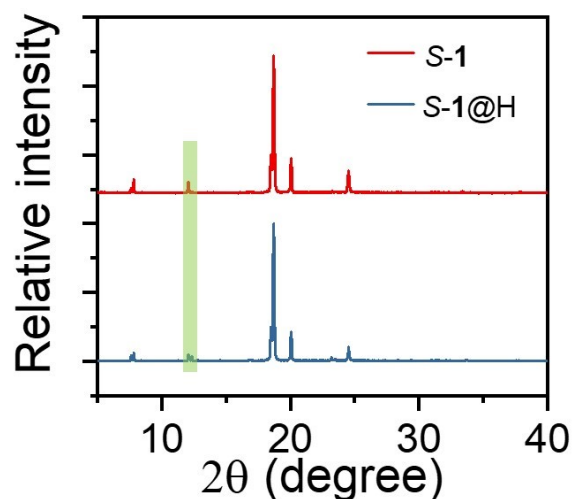


Figure S9. PXRD patterns of initial crystals *S-1* and protonated crystals *S-1@H*.

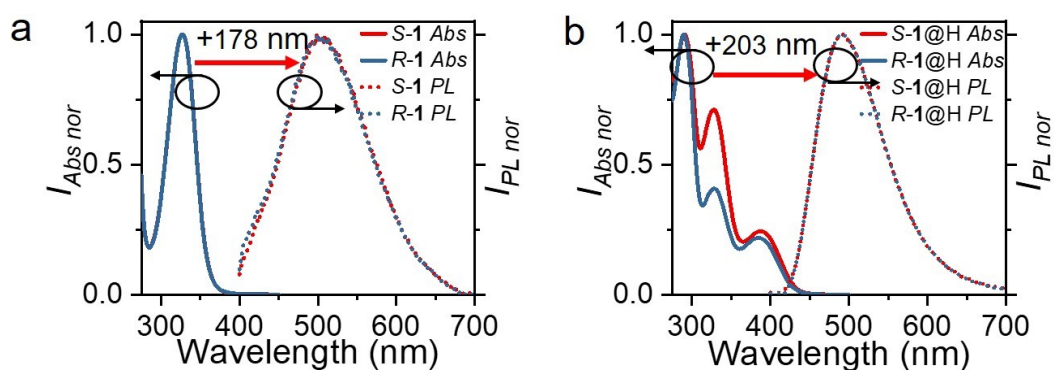


Figure S10. (a, b) Absorption and emission spectra of the compound *S-*, *R-1* (a) and *S-*, *R-1@H* (b) in DCM solution.

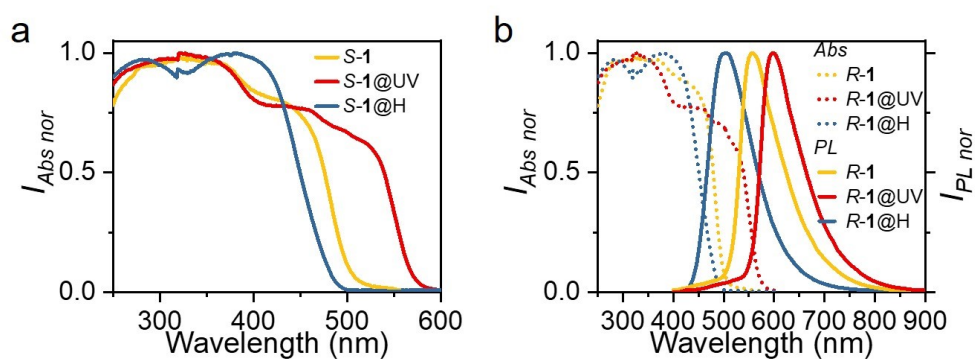


Figure S11. (a) Absorption spectra of the compound *S-1* as crystalline samples. (b) Absorption and emission spectra of the compound *R-1* as crystalline samples.

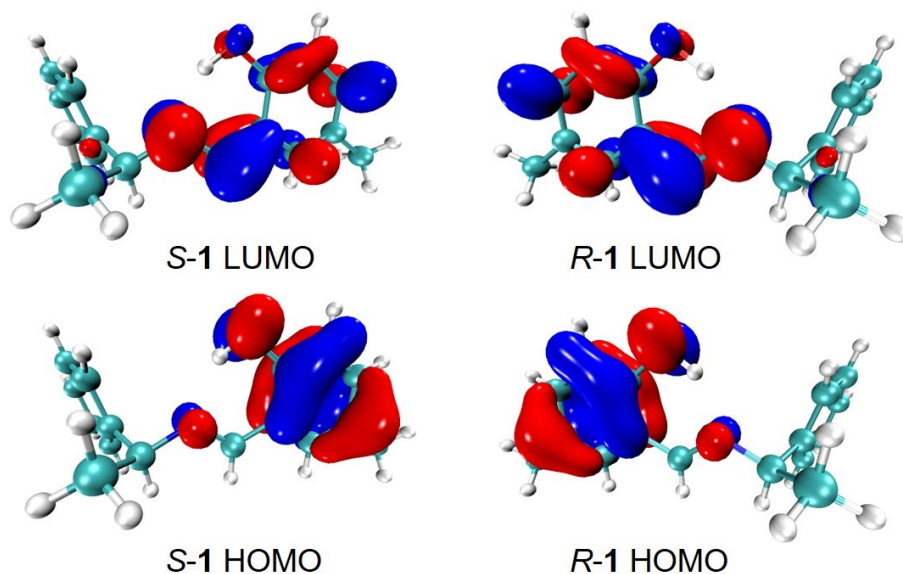


Figure S12. HOMO and LUMO for *R-1* and *S-1* molecules.

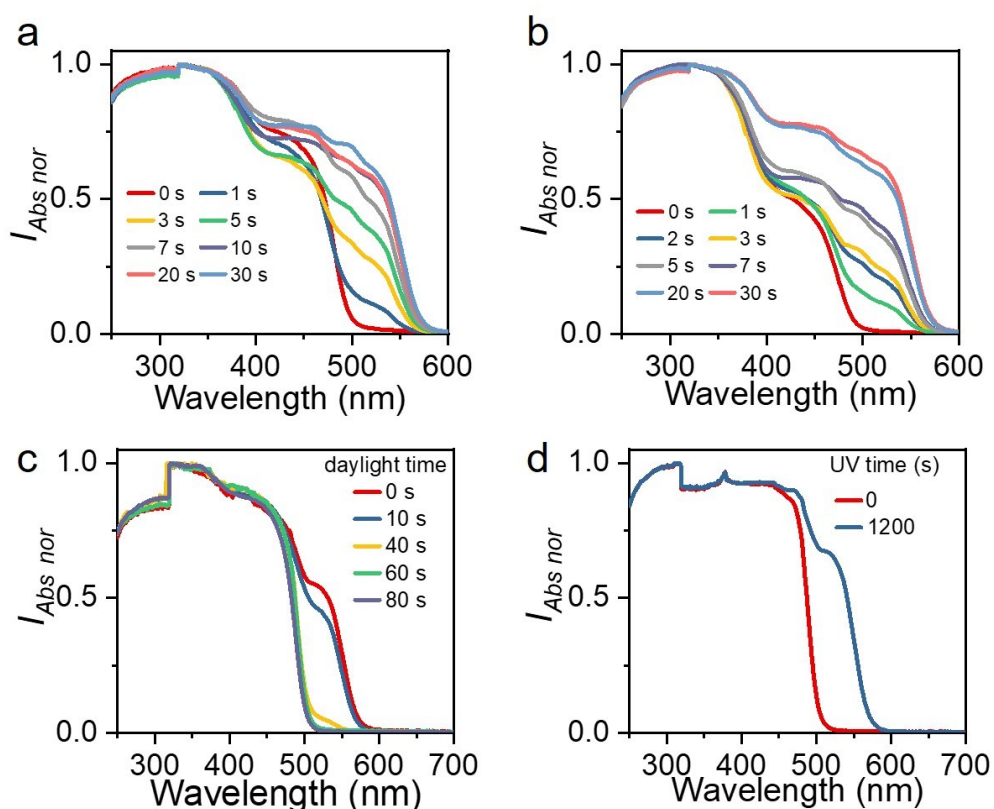


Figure S13. (a) Solid-state UV-vis absorption spectra of *S-1* recorded before and after 365 nm light irradiation for different illumination time. (b) Solid-state UV-vis absorption spectra of *R-1* recorded before and after 365 nm light irradiation for different illumination time. (c) Change of solid-state UV-vis absorption spectra of *S-1* with time after stopping 365 nm light irradiation and keeping the sample under daylight irradiation. (d) The absorption spectra of *S-1* with UV irradiation in solid state.

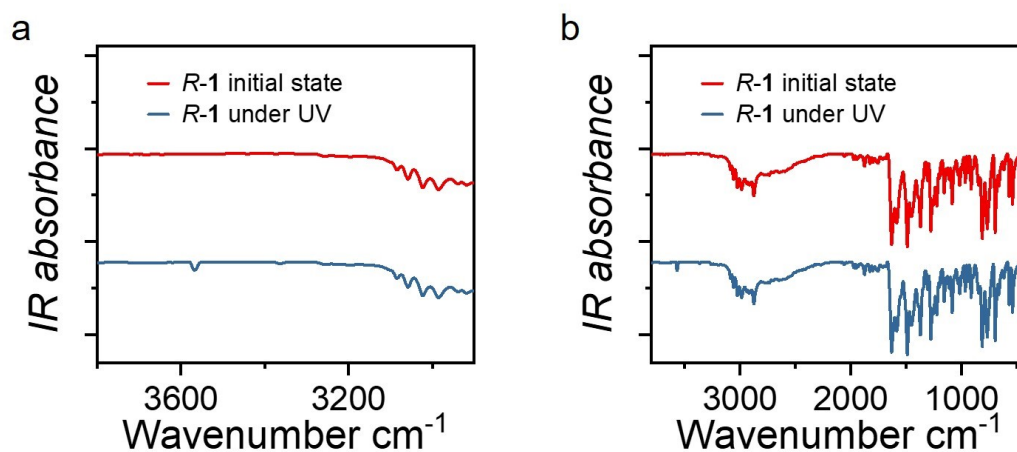


Figure S14. Experimental IR absorption spectra (a, b) of *R-1* under ambient conditions and under UV irradiation at 365 nm (panel a: spectra in the wavenumber range of 3800 to 2900 cm^{-1} ; panel b: full spectra).

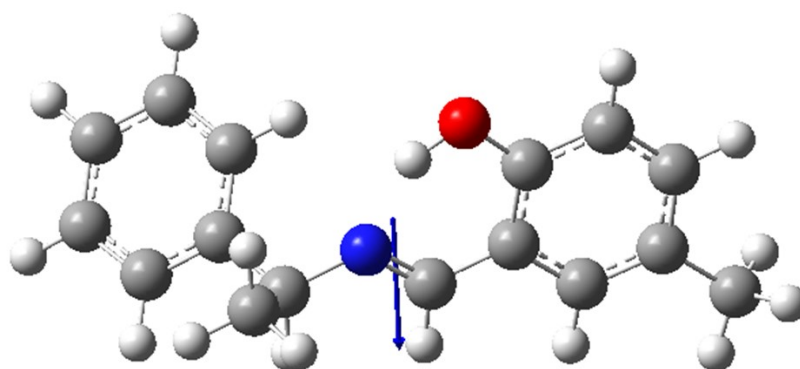


Figure S15. Molecular structure of *S-1* with enol form 2.3171 Debye.

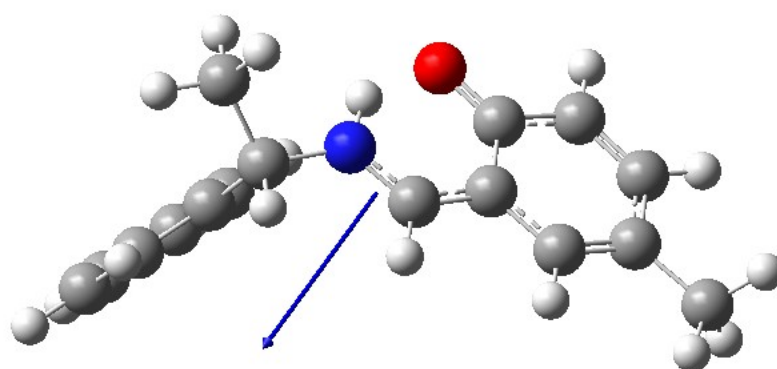


Figure S16. Molecular structure of *S-1* with *cis*-keto form 3.7678 Debye.

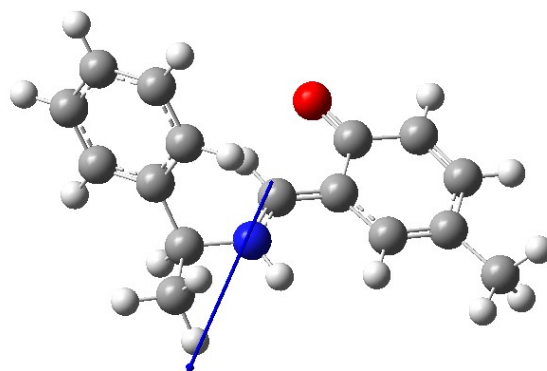


Figure S17. Molecular structure of *S-1* with *trans*-keto form 5.7812 Debye.

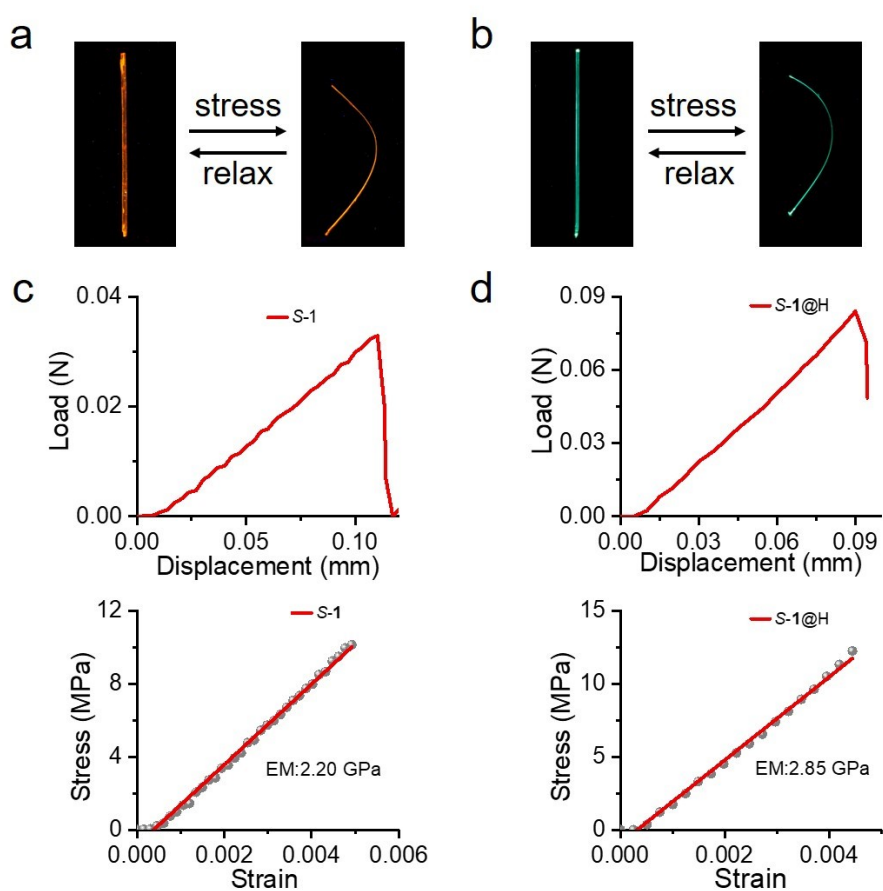


Figure S18. (a, b) Reversible bending-relaxation process of the crystals *S-1*@UV (a) and *S-1*@H (b) under 365 nm UV light. (c, d) Load-displacement curves (top) and fitted stress-strain curves (bottom) of *S-1* (c) and *S-1*@H (d) in three-point bending tests.

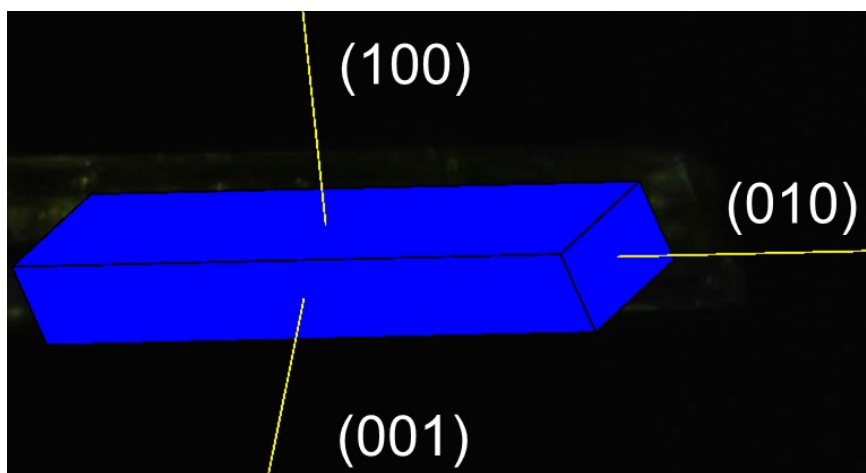


Figure S19. Face indexing for *S-1* based on X-ray diffraction.

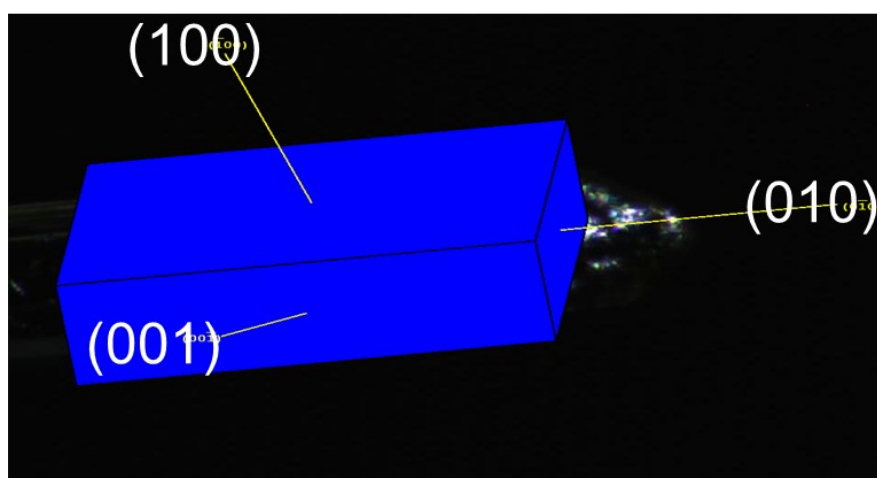


Figure S20. Face indexing for *R-1* based on X-ray diffraction.

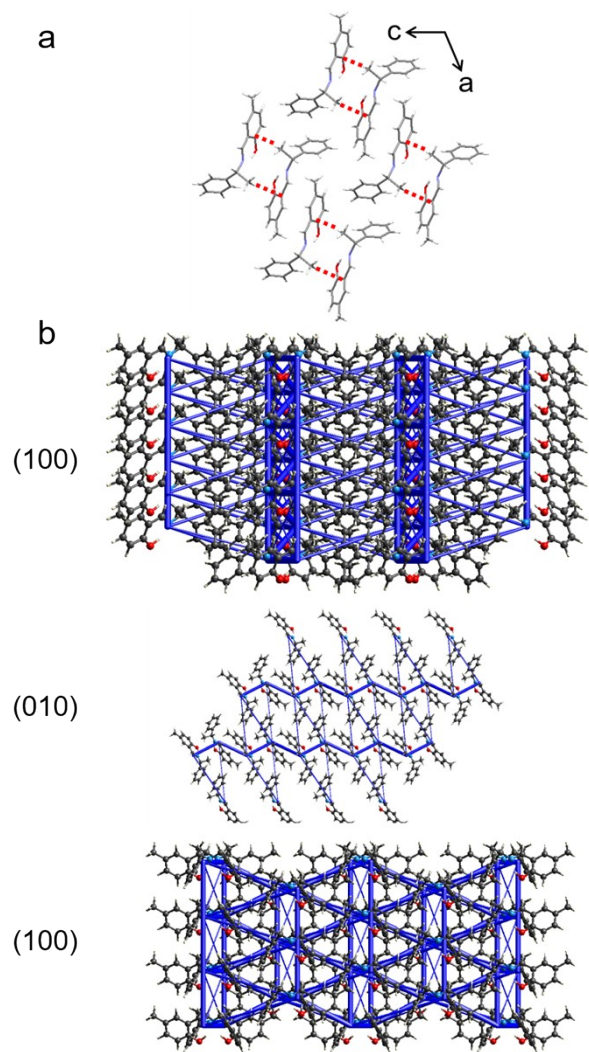


Figure S21. (a) Intermolecular interactions in *R*-1 along the *b*-axis (the red dotted line represents C–H··· π interaction). (b) Energy frameworks of crystal *R*-1 along different directions.

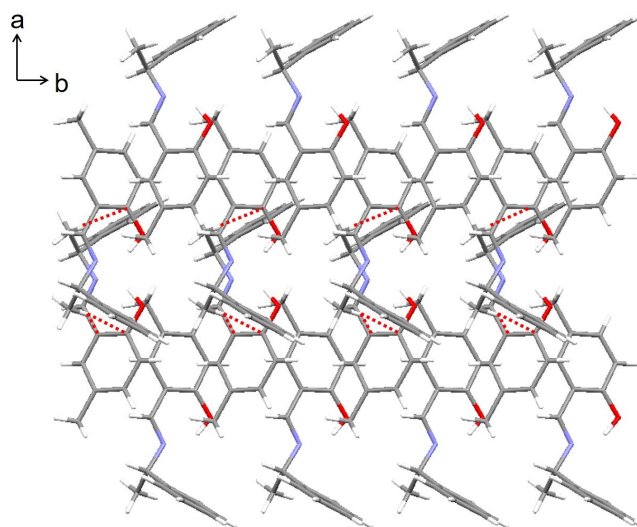


Figure S22. Molecular packing and intermolecular interactions in *S*-1. The red dotted lines show the C–H··· π interactions.

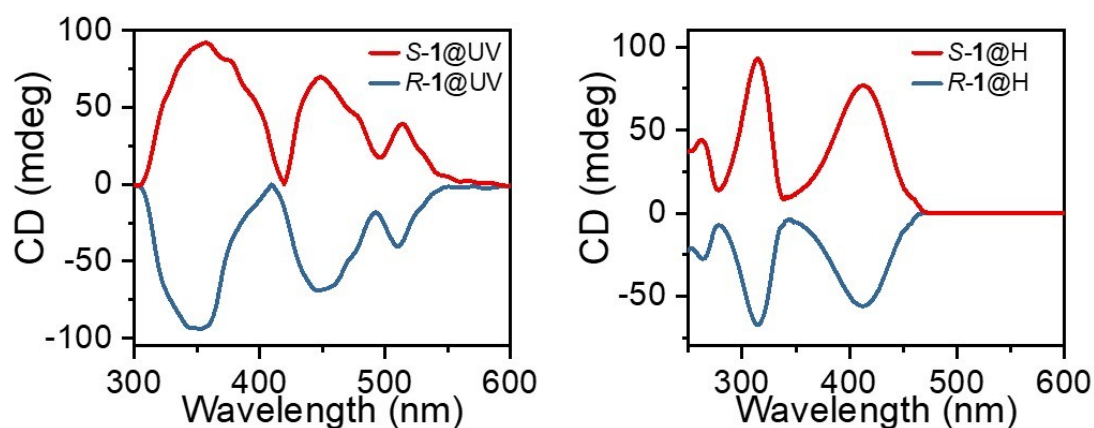


Figure S23. CD spectra of *S-1@UV*, *R-1@UV* and *S-1@H*, *R-1@H* as powder samples.

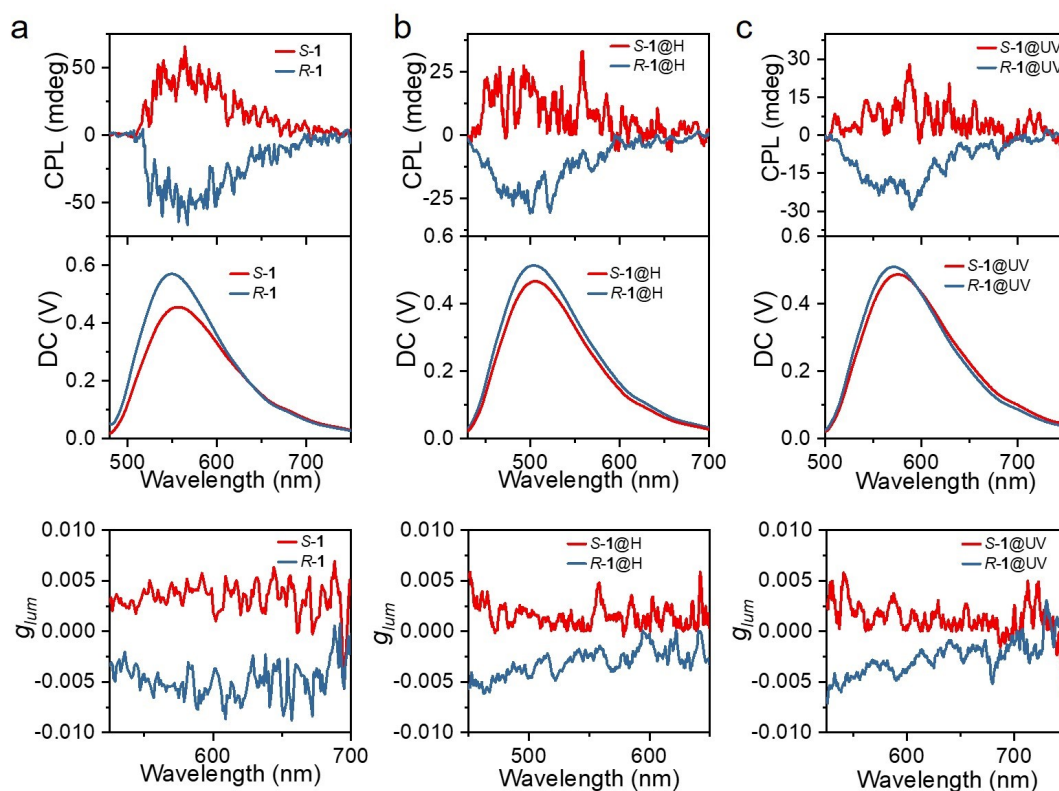


Figure S24. (a) CPL emission spectra of *S-1* and *R-1* as powder samples. (b) CPL emission spectra of *S-1@H* and *R-1@H* as powder samples. (c) CPL emission spectra of *S-1@UV* and *R-1@UV* as powder samples.

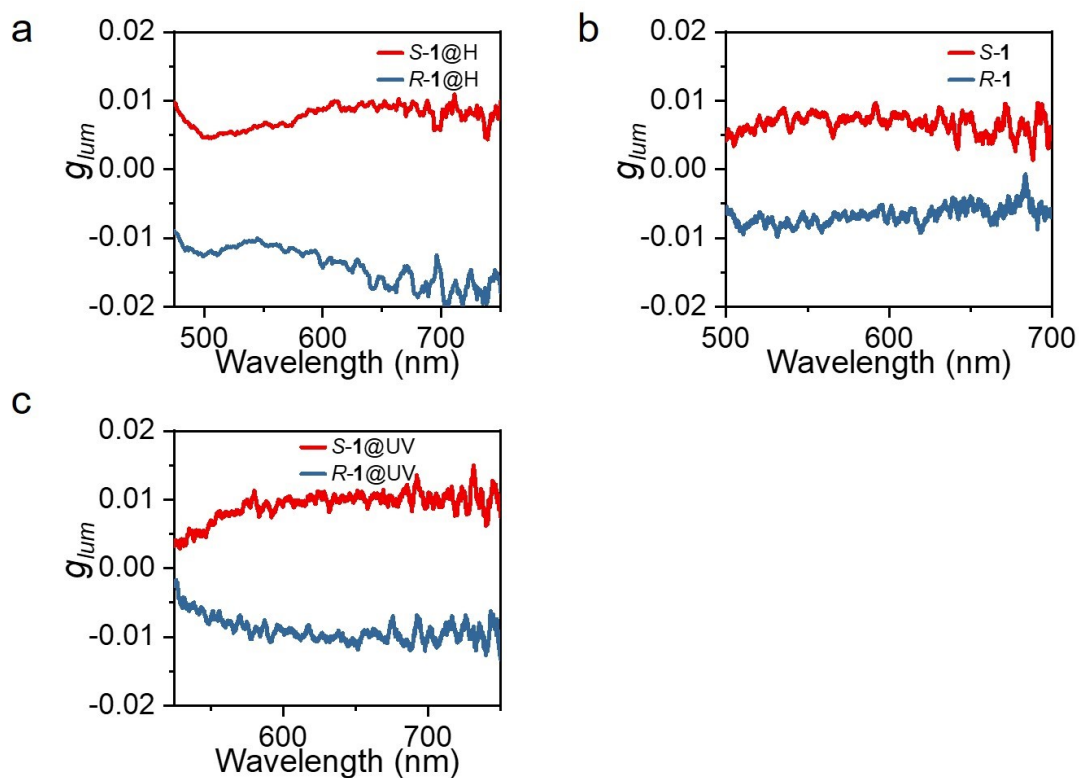


Figure S25. The g_{lum} factor versus wavelength for *S-1*@H and *R-1*@H (a), *S-1* and *R-1* (b), *S-1*@UV and *R-1*@UV (c) in single-crystal.

Table S1 Crystallographic data of crystal *S-1* and *R-1*.

Identification code	<i>S-1</i>	<i>R-1</i>
Empirical formula	C ₁₆ H ₁₇ NO	C ₁₆ H ₁₇ NO
Formula weight	239.30	239.30
Temperature/K	100.0 K	100.0 K
Crystal system	monoclinic	monoclinic
Space group	<i>C</i> 2	<i>C</i> 2
<i>a</i> /Å	20.0857(12)	20.291(2)
<i>b</i> /Å	5.8189(4)	5.8861(6)
<i>c</i> /Å	14.3076(9)	14.4945(14)
α /°	90	90
β /°	128.517(2)	128.653(4)
γ /°	90	90
Volume/Å ³	1308.39(15)	1351.9(2)
<i>Z</i>	4	4
ρ_{calc} /cm ³	1.215	1.176
μ /mm ⁻¹	0.589	0.570
<i>F</i> (000)	512.0	512.0
Crystal size/mm ³	0.20 × 0.15 × 0.13	0.22 × 0.16 × 0.12
Radiation	CuK α (λ = 1.54178)	CuK α (λ = 1.54178)
2 θ range for data collection/°	7.898 to 149.172	11.166 to 136.116

Index ranges	-24 ≤ h ≤ 24, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17	-24 ≤ h ≤ 24, -6 ≤ k ≤ 7, -17 ≤ l ≤ 17
Reflections collected	11489	10141
Independent reflections	2639	2449
Data/restraints/parameters	2639/1/169	2449/1/170
Goodness-of-fit on F ²	1.082	1.046
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0401, wR2 = 0.0975	R1 = 0.0431, wR2 = 0.1078
Final R indexes [all data]	R1 = 0.0428, wR2 = 0.1005	R1 = 0.0528, wR2 = 0.1179
Largest diff. peak/hole / e Å ⁻³	0.21/-0.25	0.12/-0.12
Flack parameter	-0.02(16)	0.0(3)

Supplementary references

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gilde, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339 – 341.

Legends for the supplementary movie

Supplementary Movie 1. The fluorescent color of the crystals gradually changed from yellow to orange-red within 30s under 365 nm UV light. When the orange-red needle-like crystal was placed in the center of the petri dish which was surrounded by cotton absorbing hydrochloric acid, the maximum emission fluorescence wavelength appeared blue-shifted, and finally, the entire crystal emits green fluorescence.