

Electronic Supplementary Information (ESI)

Photochromism and mechanism of pyrazolones in crystals: structural variations directly observed by X-ray diffraction

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1. Experimental Section

General

¹H NMR spectra were performed on an INOVA-400 NMR Spectrometer with DMSO-*d*₆ as solvent. Mass spectrum was determined with HP1100 LC-MS. Melting point was measured with a TECH XT-5 melting point apparatus. The elemental analyses were made on FLASH EA 1112 Series NCHS-O analyzer. Absorption spectra were measured on Hitachi UV-3010 spectrometer equipped with an integrating sphere accessory. Fluorescence spectra were studied using Hitachi F-4500 fluorescence Spectrophotometer. FT-IR spectra were recorded in the range 400–4000 cm⁻¹ on a BRUKER EQUINOX-55 spectrometer. X-Ray photoelectron spectra (XPS) were measured with a Perkin-Elmer PHI 5300 System. An Ultraviolet lamp (60 W) and a tungsten lamp (100 W) with wavelength cutoff filter (>420 nm) as sources for photocoloration and photobleaching, respectively. A TECH XT-5 melting point apparatus were used for thermalcoloration.

Materials

1-phenyl-3-(4-fluorophenyl)-5-pyrazolone (P4FPP) was synthesized with the method described in literature([Li, J. Y.; Wang, X. Y.; Zhao, Q. H. Chin. J. Chem. Reagen 1997, 19, 112-113](#)). 4-methylthiosemicarbazide (MTSC), 2-chlorobenzoylchloride and 4-fluorobenzoylchloride were purchased from the Aldrich Company, USA. Other materials were purchased from commercial sources, and the solvents were purified with standard procedures.

1-phenyl-3-(4-fluorophenyl)-4-(2-chlorobenzal)-5-pyrazolone (P4FP2ClBP) was synthesized with the method reported([Jensen, B. S. Acta Chem. Scand. 1959, 13, 1668-1670](#)). For P4FP2ClBP: Yield: 71%; mp. 109.4–110.6 °C; Anal. Calcd for C₂₂H₁₄N₂O₂FCl: C, 67.27; H, 3.59; N, 7.13; found: C, 66.61; H, 3.82; N, 7.20.

1-phenyl-3-(4-fluorophenyl)-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone (**1a**). P4FP2ClBP (3 mmol) and MTSC (3 mmol) were dissolved in EtOH (20 mL) together with a few drops of glacial acetic acid, and the

mixture was stirred and refluxed for 6 h at 80 °C. After cooling down to room temperature, white powders were isolated from the solution and separated by filtration. The crude product was purified by recrystallization using EtOH. Yield: 76%. mp: 201.2–202.1 °C. ¹H NMR (400 MHz, DMSO-d₆, δ): 12.342 (0.32H, O–H), 11.041 (0.62H, N2–H), 9.787 (1H, N4–H), 8.394 (1H, N5–H), 7.996–6.880 (13H, phenyl-ring), 3.049–2.916 (3H, –CH₃). ¹³C NMR (400 MHz, DMSO-d₆, δ): 181.776, 178.816, 163.802–160.333, 149.707, 148.318, 138.572–114.252, 98.950, 31.328. FT-IR (cm⁻¹) (the white powder before irradiation): 3319, 3268 ν(N–H), 1636 ν(C=N), 1608, 1563 ν(phenyl), 1598, 1461 ν(pyrazolone-ring), 941 ν(C=S); FT-IR (cm⁻¹) (the yellow powder after irradiation): 3320 3269 ν(N–H), 1671 ν(C=O), 1636 ν(C=N), 1608, 11563 ν(phenyl), 1599, 1461 ν(pyrazolone-ring), 941 ν(C=S). MS (ESI, m/z): [M + H]⁺ calcd for C₂₄H₁₉N₅OFSCl, 480.96; found, 480.1. Anal. calcd for C₂₄H₁₉N₅OFSCl: C, 60.06; H, 3.99; N, 14.59; S, 6.68; found: C, 60.22; H, 4.12; N, 14.27; S, 6.71.

X-ray crystal structure analysis

Single crystals of **1** suitable for X-ray crystallographic work were grown by slow evaporation of its ethanol solution at room temperature. The crystallographic data were collected on an imaging plate system (Rigaku R-AXIS SPIDER) with a graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073 \text{ \AA}$, ω -scans). For **1a**: A total of 17794 reflections were collected, of which 4207 reflections were independent. The number of the parameters was 345. The structure was solved by the direct method using *SHELXS-97* and refined by the full-matrix least-squares on F^2 using *SHELXL-97*. Seven non-hydrogen atoms (C17', C18', C19', C20', C21', C22' and Cl') were refined isotropically, and bond lengths and geometry of all atoms were restrained in the disorder part. The other non-H atoms were refined anisotropically. The H atoms on O and N were located from the Fourier maps and refined isotropically with bond lengths constraint. The H atoms on O and N₂ atoms were treated as disorder model in the refinement of structure **1a**, and the population of H atom on O was determined to be *ca.* 34.6% based on the occupancy of hydrogen atom.

All of the other H atoms were refined according to riding models. For **1b**: A total of 17943 reflections were collected, of which 4200 reflections were independent. The number of the parameters was 311. All non-H atoms were refined anisotropically. The H atoms on N were located from the Fourier maps and refined isotropically with bond lengths constraint. All of the other H atoms were refined according to riding models.

Table S1. Crystal data and structure refinement for **1a** and **1b**.

	1a	1b^a
empirical formula	C ₂₄ H ₁₉ N ₅ OFSCl	
formula weight	479.95	
temperature (K)	293(2)	
crystal system	monoclinic	
space group	P2 ₁ /c	
crystal size (mm ³)	0.31 × 0.19 × 0.18	
Z	4	
a (Å)	12.4255(8)	12.4127(16)
b (Å)	14.4075(8)	14.3970(18)
c (Å)	13.4165(7)	13.3934(14)
β (deg)	107.9890(10)	108.020(2)
V (Å ³)	2284.4(2)	2276.1(5)
density calcd (g/cm ³)	1.396	1.401
θ range for data collection	3.04–27.46°	3.04–27.51°
reflections collected/unique	17794 / 4207 [R _{int} = 0.0436]	17943 / 4200 [R _{int} = 0.0477]
refinement method		Full-matrix least-squares on F ²
data/restraints/parameters	4207 / 28 / 345	4200 / 4 / 311
goodness-of-fit on F ²	1.097	1.076
R indices [I > 2 σ (I)]	R ₁ = 0.0706, wR ₂ = 0.1866	R ₁ = 0.0666, wR ₂ = 0.1951
R indices [all data]	R ₁ = 0.1102, wR ₂ = 0.2514	R ₁ = 0.0949, wR ₂ = 0.2288
largest diff. peak and hole	0.442 and -0.502 e Å ⁻³	0.949 and -0.588 e Å ⁻³

^aTo increase the population of the K-form in single crystal, the sample was heated at 180 °C other than irradiated by 365 nm light.

Table S2. Selected bond lengths (\AA) and bond angles ($^\circ$) of **1**.

1a		1b	
Bond length			
Cl-C(22)	1.726(3)	Cl-C(22)	1.727(3)
S-C(23)	1.698(4)	S-C(23)	1.693(4)
F-C(13)	1.368(5)	F-C(13)	1.364(5)
O-C(7)	1.249(5)	O-C(7)	1.235(4)
N(1)-N(2)	1.388(5)	N(1)-N(2)	1.378(4)
N(1)-C(7)	1.385(5)	N(1)-C(7)	1.394(4)
N(2)-C(9)	1.360(5)	N(2)-C(9)	1.357(4)
C(7)-C(8)	1.436(5)	C(7)-C(8)	1.440(5)
C(8)-C(9)	1.381(5)	C(8)-C(9)	1.382(5)
N(3)-C(16)	1.295(5)	N(3)-C(16)	1.292(4)
N(3)-N(4)	1.386(4)	N(3)-N(4)	1.366(4)
N(4)-C(23)	1.345(5)	N(4)-C(23)	1.359(4)
N(5)-C(23)	1.321(5)	N(5)-C(23)	1.318(5)
N(5)-C(24)	1.441(6)	N(5)-C(24)	1.448(5)
Bond angles			
O-C(7)-N(1)	122.8(4)	O-C(7)-N(1)	123.8(3)
O-C(7)-C(8)	130.5(4)	O-C(7)-C(8)	130.8(3)
N(2)-N(1)-C(7)	108.5(3)	N(2)-N(1)-C(7)	109.1(3)
N(2)-N(1)-C(6)	120.4(3)	N(2)-N(1)-C(6)	120.9(3)
C(7)-N(1)-C(6)	128.6(3)	C(7)-N(1)-C(6)	127.6(3)
C(9)-N(2)-N(1)	108.3(3)	C(9)-N(2)-N(1)	108.7(3)
N(1)-C(7)-C(8)	106.7(3)	N(1)-C(7)-C(8)	105.4(3)
N(2)-C(9)-C(8)	109.7(3)	N(2)-C(9)-C(8)	109.2(3)
N(2)-C(9)-C(10)	118.2(3)	N(2)-C(9)-C(10)	118.4(3)
N(3)-C(16)-C(8)	127.1(3)	N(3)-C(16)-C(8)	127.0(3)
N(5)-C(23)-N(4)	118.5(4)	N(5)-C(23)-N(4)	117.8(3)
N(5)-C(23)-S	123.9(3)	N(5)-C(23)-S	124.4(3)
N(4)-C(23)-S	117.5(3)	N(4)-C(23)-S	117.8(3)

Table S3. Intra- and intermolecular hydrogen bonding geometry in *E*-form crystal.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	(D–H···A) (°)
N(4)–H(4N)···O	0.863(10)	1.843(14)	2.699(5)	171(6)
O–H(1O)···N(4)	0.821(10)	2.03(15)	2.699(5)	139(20)
N(2)–H(2N)···S ^{#1}	0.860(10)	2.387(12)	3.244(4)	174(5)
N(5)–H(5N)···O ^{#2}	0.861(10)	2.46(4)	3.044(5)	125(4)
N(5)–H(5N)···N(3)	0.861(10)	2.28(5)	2.648(5)	106(4)

Symmetry codes: #1 -x+1, -y+1, -z+1; #2 x, -y+3/2, z+1/2

Table S4. Intra- and intermolecular hydrogen bonding geometry in *K*-form crystal.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	(D–H···A) (°)
N(4)–H(4N)···O	0.861(10)	1.884(17)	2.695(4)	156(3)
N(2)–H(2N)···S ^{#1}	0.860(10)	2.386(12)	3.240(3)	172(4)
N(5)–H(5N)···O ^{#2}	0.855(10)	2.58(4)	3.033(4)	115(4)
N(5)–H(5N)···N(3)	0.855(10)	2.10(4)	2.640(4)	121(4)

Symmetry codes: #1 -x+1, -y+1, -z+1; #2 x, -y+3/2, z+1/2

2. Photochromic properties of 1 in crystalline state

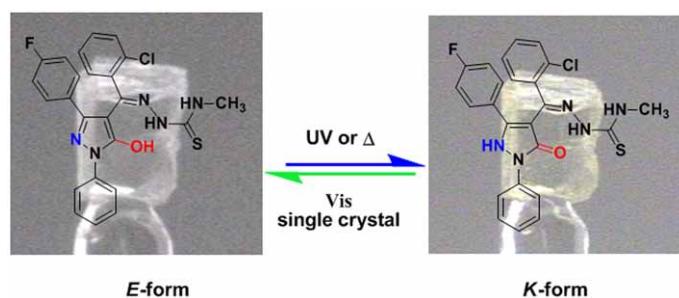


Fig. S1 Photochromism of 1 in single crystal under UV light irradiation or heating.

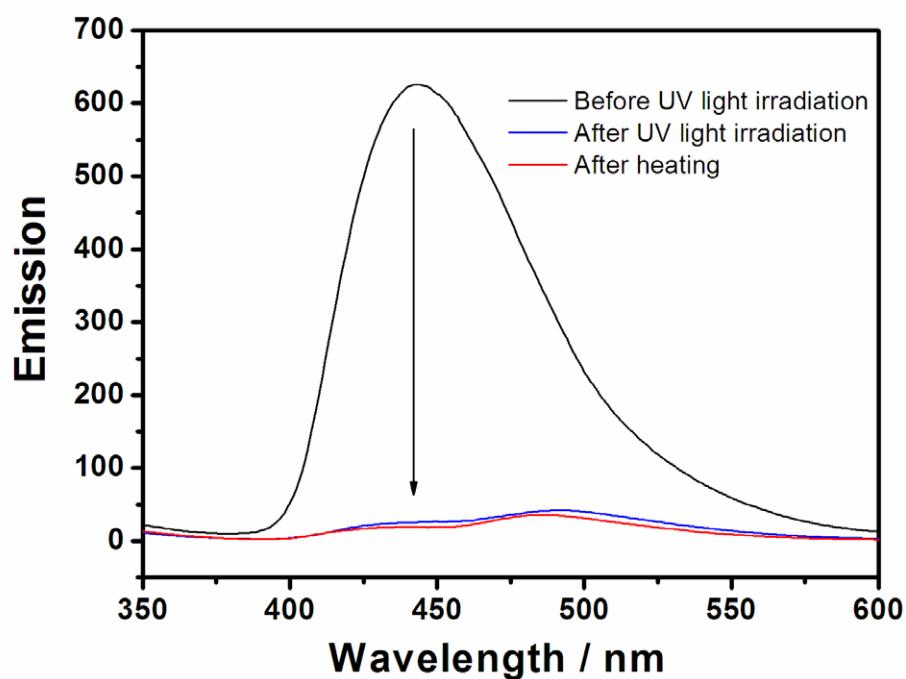


Fig. S2 Fluorescence changes of **1** in crystalline powders before irradiated by UV light, after irradiated by UV light for several hours and after heating at 180 °C ($\lambda_{\text{ex}} = 320 \text{ nm}$).

3. IR and XPS spectra of **1**

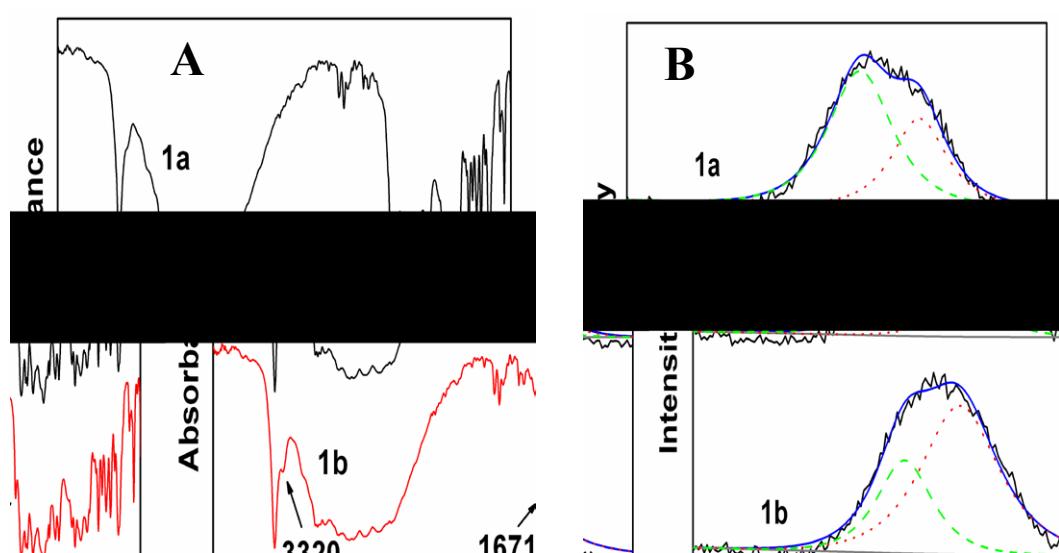


Fig. S3 (A) FT-IR spectra of **1** before and after UV irradiation and (B) O1s spectra (XPS) of **1** before and after heating. The colored lines in (B) show the results of curve fitting.

4. hydrogen bonds of 1

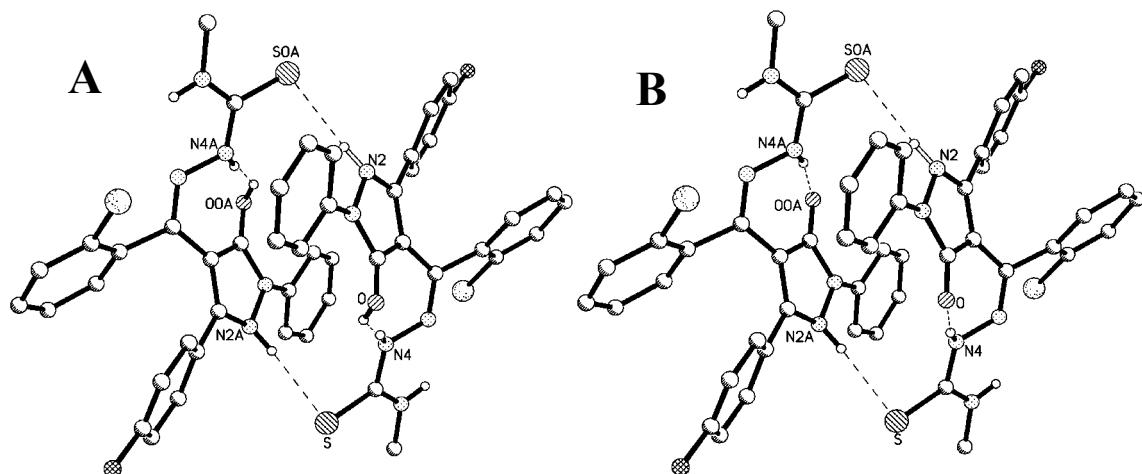


Fig. S4 (A) Hydrogen bond connection diagram of **1a** and (B) **1b** (Hydrogen atoms of carbon atoms and disordered part are omitted).