Electronic Supplementary Information (ESI)

Solid-state photochromism of pyrazolones with highly improved sensitivity, fatigue resistance and reversible fluorescent switching properties

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Figure S1. Photochromic reaction of single crystal of **1** under irradiation with 365 nm light.

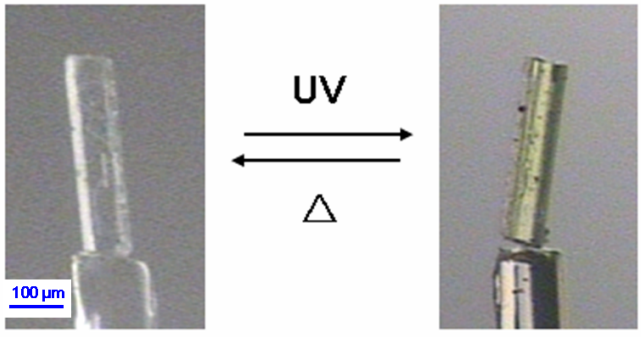

Figure S2. Normalized emission changes of **1** with UV irradiation (λ_{ex} = 260 nm)

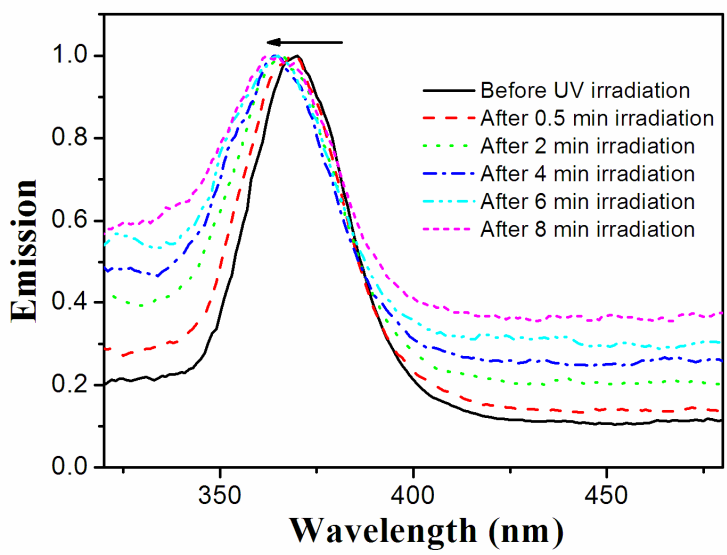

Figure S3. Normalized emission changes of **2** with UV irradiation (λ_{ex} = 260 nm)

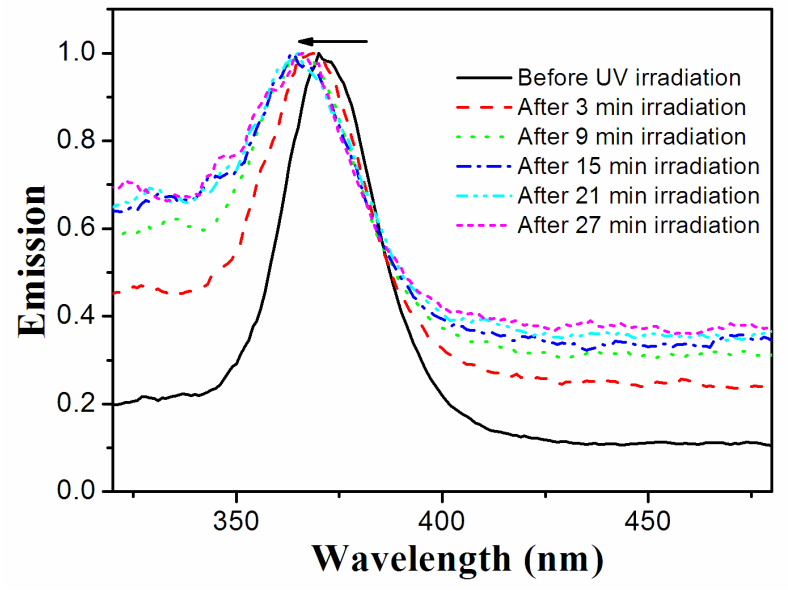

Figure S4. X-ray diffraction data of **1a** at room temperature.

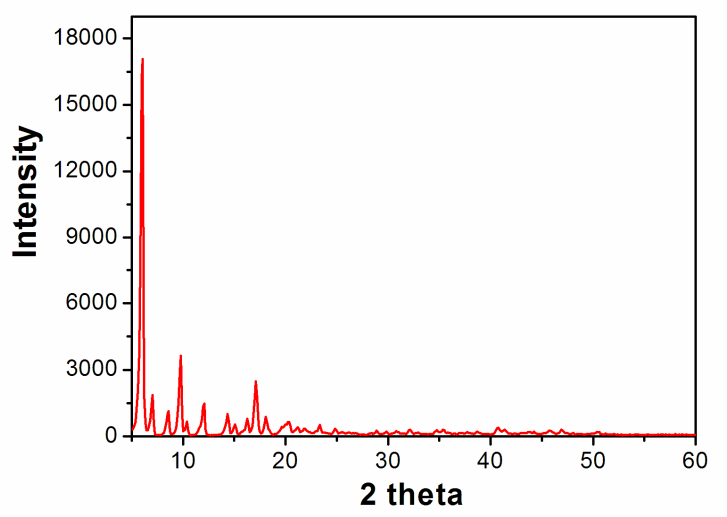

Figure S5. X-ray diffraction data of **2a** at room temperature.

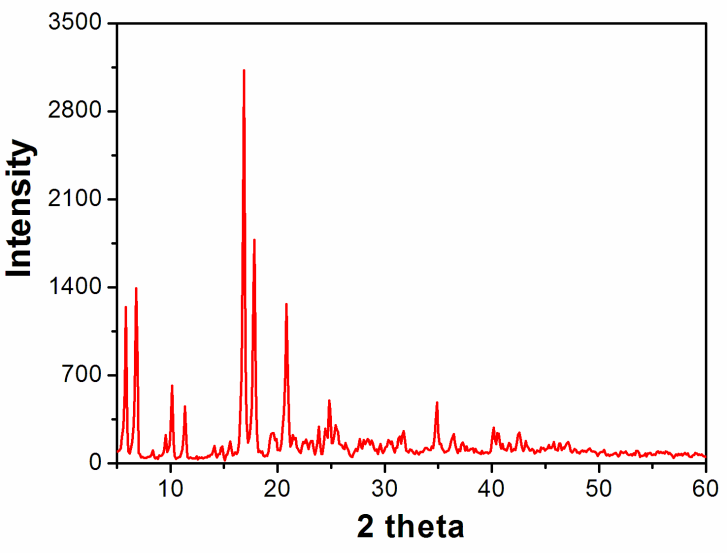

Table S1. Crystal data and structure refinement for **1a**

Empirical formula	$C_{29}H_{22}N_5O2Cl$
Formula weight	507.97
Temperature	153(2) *K*
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.982(2) Å α = 90º
	b = 18.017(3) Å β = 106.586(1)º
	c = 26.297(6) Å γ = 90º
Volume	4986.39(17) $Å^3$
Z	8
Calculated density	1.353 g/cm^3
Absorption coefficient	0.191 mm^{-1}
F(000)	2112
Crystal size	0.48 × 0.10 × 0.10 mm
Theta range for data collection	3.07–27.48º
Limiting indices	$-13 \le h \le 12$, $-21 \le k \le 21$, $-31 \le l \le 31$
Reflections collected / unique	61422 / 9279 [R_{int} = 0.0569]
Absorption correction	Empirical
Max. and min. transmission	0.9812 and 0.8141
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9279 / 6 / 692
Goodness-of-fit on F^2	1.112
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0486, wR_2 = 0.1215
R indices (all data)	R_1 = 0.0748, wR_2 = 0.1548
Extinction coefficient	0.0050(5)
Largest diff. peak and hole	0.371 and -0.506 e $Å^{-3}$

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for **1a**

Molecule A		Molecule B	
Cl(1A)-C(20A)	1.731(3)	Cl(1B)-C(20B)	1.742(3)
O(1A)-C(7A)	1.336(3)	O(1B)-C(7B)	1.328(3)
O(2A)-C(23A)	1.252(3)	O(2B)-C(23B)	1.244(3)
N(1A)-C(7A)	1.360(3)	N(1B)-C(7B)	1.368(3)
N(1A)-N(2A)	1.371(3)	N(1B)-N(2B)	1.379(3)
N(1A)-C(6A)	1.426(3)	N(1B)-C(6B)	1.420(3)
N(2A)-C(9A)	1.331(3)	N(2B)-C(9B)	1.323(3)
N(3A)-C(16A)	1.295(3)	N(3B)-C(16B)	1.293(3)
N(3A)-N(4A)	1.377(3)	N(3B)-N(4B)	1.375(3)
N(4A)-C(23A)	1.371(3)	N(4B)-C(23B)	1.373(3)
N(5A)-C(23A)	1.338(3)	N(5B)-C(23B)	1.340(3)
N(5A)-C(24A)	1.423(3)	N(5B)-C(24B)	1.414(3)
C(7A)-C(8A)	1.380(3)	C(7B)-C(8B)	1.382(3)
C(8A)-C(9A)	1.429(3)	C(8B)-C(9B)	1.423(3)
C(8A)-C(16A)	1.467(3)	C(8B)-C(16B)	1.477(3)
C(9A)-C(10A)	1.463(3)	C(9B)-C(10B)	1.475(3)
C(16A)-C(17A)	1.492(3)	C(16B)-C(17B)	1.486(3)
C(7A)-O(1A)-H(1AO)	112(3)	C(7B)-O(1B)-H(1BO)	118(3)
C(7A)-N(1A)-N(2A)	111.33(19)	C(7B)-N(1B)-N(2B)	111.02(18)
C(7A)-N(1A)-C(6A)	128.7(2)	C(7B)-N(1B)-C(6B)	129.54(19)

N(2A)-N(1A)-C(6A)	120.00(18)	N(2B)-N(1B)-C(6B)	119.17(19)
C(9A)-N(2A)-N(1A)	105.13(18)	C(9B)-N(2B)-N(1B)	105.06(18)
C(16A)-N(3A)-N(4A)	118.85(19)	C(16B)-N(3B)-N(4B)	118.35(19)
C(23A)-N(4A)-N(3A)	116.55(19)	C(23B)-N(4B)-N(3B)	118.29(19)
C(23A)-N(5A)-C(24A)	129.7(2)	C(23B)-N(5B)-C(24B)	128.3(2)
C(5A)-C(6A)-N(1A)	118.7(2)	C(5B)-C(6B)-N(1B)	118.8(2)
O(1A)-C(7A)-N(1A)	118.6(2)	O(1B)-C(7B)-N(1B)	119.0(2)
O(1A)-C(7A)-C(8A)	133.5(2)	O(1B)-C(7B)-C(8B)	133.4(2)
N(1A)-C(7A)-C(8A)	107.91(19)	N(1B)-C(7B)-C(8B)	107.58(19)
C(7A)-C(8A)-C(9A)	104.00(19)	C(7B)-C(8B)-C(9B)	104.1(2)
C(7A)-C(8A)-C(16A)	128.5(2)	C(7B)-C(8B)-C(16B)	128.9(2)
C(9A)-C(8A)-C(16A)	127.5(2)	C(9B)-C(8B)-C(16B)	126.7(2)
N(2A)-C(9A)-C(8A)	111.6(2)	N(2B)-C(9B)-C(8B)	112.17(19)
N(2A)-C(9A)-C(10A)	119.1(2)	N(2B)-C(9B)-C(10B)	119.6(2)
N(3A)-C(16A)-C(8A)	126.0(2)	N(3B)-C(16B)-C(8B)	125.7(2)
N(3A)-C(16A)-C(17A)	113.1(2)	N(3B)-C(16B)-C(17B)	115.3(2)
C(8A)-C(16A)-C(17A)	120.91(19)	C(8B)-C(16B)-C(17B)	119.0(2)
C(22A)-C(17A)-C(18A)	119.2(2)	C(22B)-C(17B)-C(16B)	120.8(2)
O(2A)-C(23A)-N(5A)	125.4(2)	O(2B)-C(23B)-N(5B)	124.2(2)
O(2A)-C(23A)-N(4A)	119.7(2)	O(2B)-C(23B)-N(4B)	120.0(2)
N(5A)-C(23A)-N(4A)	114.9(2)	N(5B)-C(23B)-N(4B)	115.8(2)

Table S3. Hydrogen Bonds for **1a**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	(D–H···A) (º)
O(1A)-H(1AO)···O(2B)	0.830(10)	1.735(12)	2.560(2)	173(4)
O(1B)-H(1BO)···O(2A)	0.827(10)	1.770(12)	2.589(2)	170(4)
N(4A)-H(4AN)···O(2A) [#1]	0.862(10)	2.331(16)	3.114(3)	151(2)
N(5A)-H(5AN)···N(3A)	0.867(10)	2.07(3)	2.554(3)	115(2)
N(4B)-H(4BN)···O(2B) [#2]	0.870(10)	2.37(2)	3.050(3)	135(2)
N(5B)-H(5BN) ···N(3B)	0.867(10)	2.15(2)	2.607(3)	112.7(19)

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