Supplementary Information

Solid-state photochromic behavior of pyrazolone 4-phenylthiosemicarbazones

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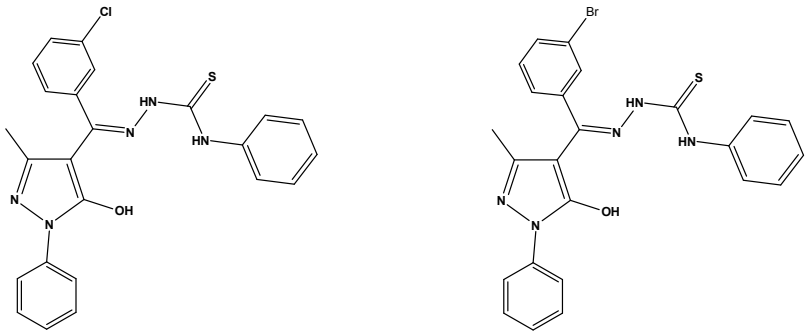

2Cl **3Br**

Figure S1. Structural formulas of 2Cl and 3Br.

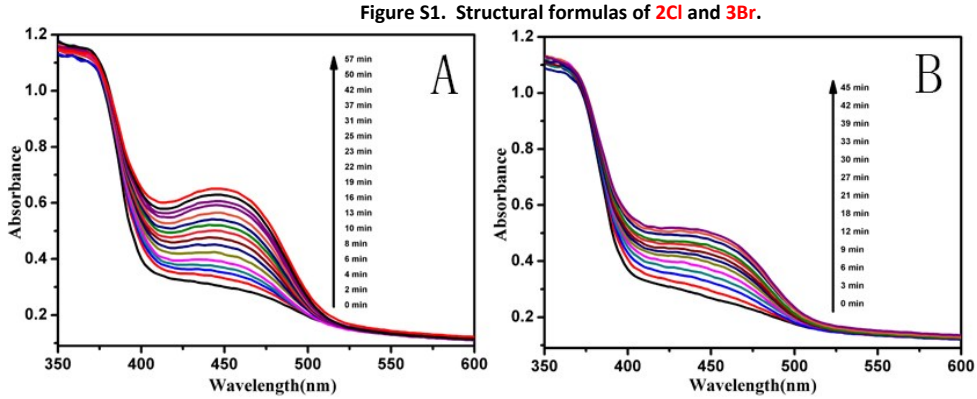

Figure S2. UV-Vis reflection spectra of two solid powders (A: 2Cl, B: 3Br) upon the irradiation of 365 nm light.

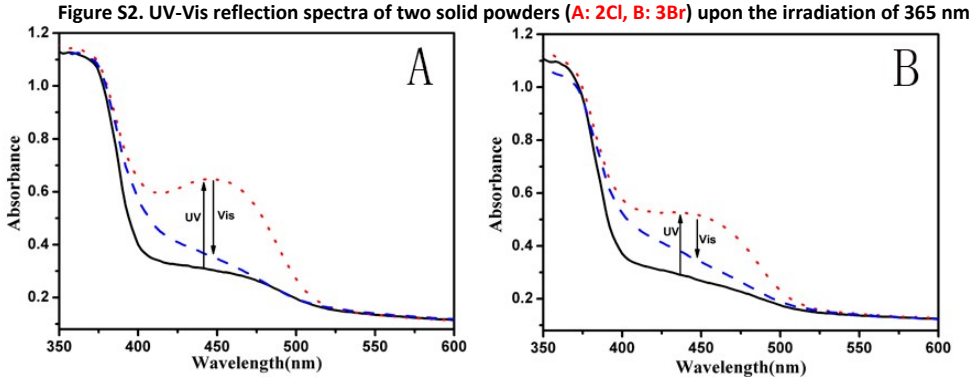

Figure S3. Absorption spectra of solid powders 2Cl (A) and solid powders 3Br (B) before (solid line) and after the irradiation of 365 nm light at room temperature (dotted line), and then after the irradiation of visible light (dashed line).

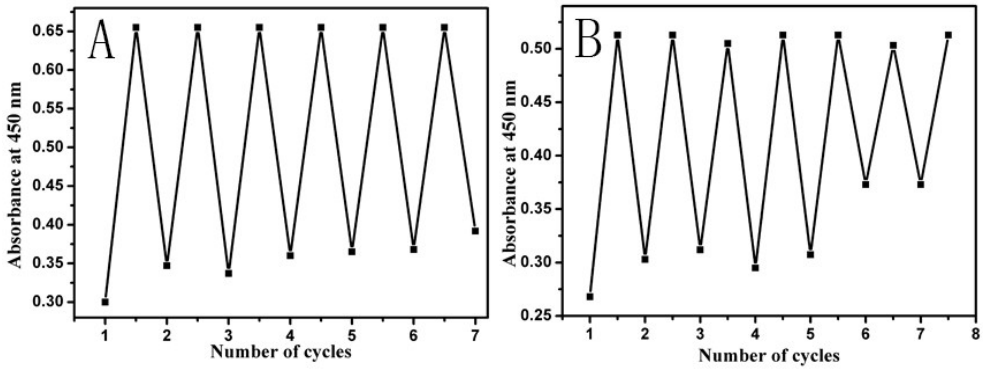

Figure S4. Photoswitching cycles of 2Cl (A) and 3Br (B) in solid state under irradiation of alternating 365 nm light and visible light.

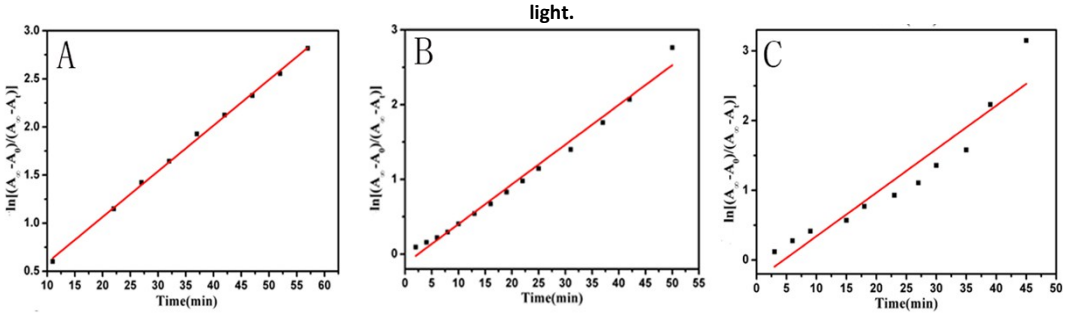

Figure S5. First-order kinetic plot of photoisomerization reaction of 1F (A), 2Cl (B) and 3Br (C) in solid state induced by 365 nm light at room temperature.

Table S1. Crystal data and structure refinement for 1F

1F	
Empirical formula	$C_{24}H_{20}FN_5OS$
Formula weight	445.52
Temperature (K)	296
Wavelength	0.71073 Å
Crystal system,	Monoclinic
space group	*P*2(1) / *n*
Unit cell dimensions	*a* = 10.700(2)Å
	b = 14.421(3)Å
	c = 14.701(3) Å
	α= 90 deg
	β= 101.754(3) deg
	γ= 90 deg
Volume	2220.9(7) $Å^3$
Calculated density	1.332mg/m^3
Z	4

Theta range for data collection	2.16 to 25.00 deg
Completeness to theta = 25.00	97.9 %
Limiting indices	-12≤*h*≤9, -17≤*k*≤16, -15≤*l*≤17
Reflections collected / uniqu	10935 / 3840 [R_{int} = 0.0517]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3840 / 0 / 291
Goodness-of-fit on F^2	0.859
Absorption coefficient	0.181 mm^{-1}
F(000)	928
Final R indices [I>2sigma(I)]	R1 = 0.0670, wR2 = 0.1670
R indices (all data)	R_1 = 0.1160, wR_2 = 0.1970
Extinction coefficient	0.0031(8)

Table S2. Selected bond lengths (Å) and angles (^{0}) for 1F

Bond lengths			
C(1)-C(2)	1.377(7)	C(14)-C(15)	1.363(7)
C(1)-C(6)	1.396(6)	C(14)-F(1)	1.366(6)
C(1)-H(1)	0.93	C(15)-C(16)	1.372(7)
C(2)-C(3)	1.370(8)	C(15)-H(15)	0.93
C(2)-H(2)	0.93	C(16)-C(17)	1.375(7)
C(3)-C(4)	1.381(8)	C(16)-H(16)	0.93
C(3)-H(3)	0.93	C(17)-H(17)	0.93
C(4)-C(5)	1.388(7)	C(18)-N(4)	1.342(5)
C(4)-H(4)	0.93	C(18)-N(5)	1.333(5)
C(5)-C(6)	1.361(7)	C(18)-S(1)	1.675(5)
C(5)-H(5)	0.93	C(19)-C(24)	1.362(7)
C(6)-N(1)	1.421(5)	C(19)-C(20)	1.373(7)
C(7)-C(9)	1.370(6)	C(19)-N(5)	1.426(5)
C(7)-N(2)	1.340(5)	C(20)-C(21)	1.371(7)
C(7)-C(8)	1.502(6)	C(20)-H(20)	0.93
C(8)-H(8A)	0.96	C(21)-C(22)	1.362(9)
C(8)-H(8B)	0.96	C(21)-H(21)	0.93
C(8)-H(8C)	0.96	C(22)-C(23)	1.372(9)
C(9)-C(10)	1.425(6)	C(22)-H(22)	0.93

C(9)-C(11)	1.469(5)	C(23)-C(24)	1.404(7)
C(10)-O(1)	1.251(5)	C(23)-H(23)	0.93
C(10)-N(1)	1.376(5)	C(24)-H(24)	0.93
C(11)-N(3)	1.296(5)	N(1)-N(2)	1.389(5)
C(11)-C(12)	1.488(6)	N(2)-H(2A)	0.86
C(12)-C(17)	1.386(6)	N(3)-N(4)	1.377(5)
C(12)-C(13)	1.385(6)	N(4)-H(4A)	0.86
C(13)-C(14)	1.366(7)	N(5)-H(5A)	0.86
C(13)-H(13)	0.93		
Bond angles			
C(2)-C(1)-C(6)	119.0(5)	C(13)-C(14)-F(1)	118.0(5)
C(2)-C(1)-H(1)	120.5	C(14)-C(15)-C(16)	117.9(5)
C(6)-C(1)-H(1)	120.5	C(14)-C(15)-H(15)	121
C(1)-C(2)-C(3)	120.1(5)	C(16)-C(15)-H(15)	121
C(1)-C(2)-H(2)	120	C(15)-C(16)-C(17)	120.4(5)
C(3)-C(2)-H(2)	120	C(15)-C(16)-H(16)	119.8
C(2)-C(3)-C(4)	120.5(5)	C(17)-C(16)-H(16)	119.8
C(2)-C(3)-H(3)	119.7	C(16)-C(17)-C(12)	120.7(5)
C(4)-C(3)-H(3)	119.7	C(16)-C(17)-H(17)	119.6
C(5)-C(4)-C(3)	120.0(6)	C(12)-C(17)-H(17)	119.6
C(5)-C(4)-H(4)	120	N(4)-C(18)-N(5)	115.4(4)
C(3)-C(4)-H(4)	120	N(4)-C(18)-S(1)	118.5(3)
C(6)-C(5)-C(4)	119.1(5)	N(5)-C(18)-S(1)	126.1(3)
C(6)-C(5)-H(5)	120.5	C(24)-C(19)-C(20)	120.4(5)
C(4)-C(5)-H(5)	120.5	C(24)-C(19)-N(5)	122.7(5)
C(5)-C(6)-N(1)	119.1(4)	C(20)-C(19)-N(5)	116.8(4)
C(5)-C(6)-C(1)	121.3(4)	C(21)-C(20)-C(19)	120.6(6)
N(1)-C(6)-C(1)	119.6(4)	C(21)-C(20)-H(20)	119.7
C(9)-C(7)-N(2)	109.3(4)	C(19)-C(20)-H(20)	119.7
C(9)-C(7)-C(8)	133.7(4)	C(20)-C(21)-C(22)	119.9(6)
N(2)-C(7)-C(8)	117.0(4)	C(20)-C(21)-H(21)	120
C(7)-C(8)-H(8A)	109.5	C(22)-C(21)-H(21)	120
C(7)-C(8)-H(8B)	109.5	C(21)-C(22)-C(23)	120.0(6)

H(8A)-C(8)-H(8B)	109.5	C(21)-C(22)-H(22)	120
C(7)-C(8)-H(8C)	109.5	C(23)-C(22)-H(22)	120
H(8A)-C(8)-H(8C)	109.5	C(22)-C(23)-C(24)	120.2(6)
H(8B)-C(8)-H(8C)	109.5	C(22)-C(23)-H(23)	119.9
C(7)-C(9)-C(10)	107.2(3)	C(24)-C(23)-H(23)	119.9
C(7)-C(9)-C(11)	125.1(4)	C(19)-C(24)-C(23)	118.8(6)
C(10)-C(9)-C(11)	127.7(4)	C(19)-C(24)-H(24)	120.6
O(1)-C(10)-N(1)	122.7(4)	C(23)-C(24)-H(24)	120.6
O(1)-C(10)-C(9)	130.8(4)	C(10)-N(1)-N(2)	108.0(3)
N(1)-C(10)-C(9)	106.4(4)	C(10)-N(1)-C(6)	129.4(4)
N(3)-C(11)-C(9)	128.0(4)	N(2)-N(1)-C(6)	120.3(3)
N(3)-C(11)-C(12)	114.0(4)	C(7)-N(2)-N(1)	108.9(3)
C(9)-C(11)-C(12)	118.0(4)	C(7)-N(2)-H(2A)	125.6
C(17)-C(12)-C(13)	119.0(4)	N(1)-N(2)-H(2A)	125.6
C(17)-C(12)-C(11)	119.9(4)	C(11)-N(3)-N(4)	118.2(3)
C(13)-C(12)-C(11)	121.0(4)	C(18)-N(4)-N(3)	118.7(3)
C(14)-C(13)-C(12)	118.4(5)	C(18)-N(4)-H(4A)	120.7
C(14)-C(13)-H(13)	120.8	N(3)-N(4)-H(4A)	120.7
C(12)-C(13)-H(13)	120.8	C(18)-N(5)-C(19)	129.3(4)
C(15)-C(14)-C(13)	123.4(5)	C(18)-N(5)-H(5A)	115.4
C(15)-C(14)-F(1)	118.6(5)	C(19)-N(5)-H(5A)	115.4

Table S3. Hydrogen bonds for 1F (distance Å and angle º)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2 - H1B...S1	1.00(4)	2.23(4)	3.234(3)	178(5)
N4 - H4A...O1	0.86	1.99	2.702(4)	140.00