Photo-switch and INHIBIT logic gate based on two pyrazolone thiosemicarbazone derivatives†

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Received (in Victoria, Australia) 27th April 2009, Accepted 3rd September 2009
First published as an Advance Article on the web 30th September 2009
DOI: 10.1039/b908326j

Two novel compounds containing a pyrazolone-ring unit, *i.e.* 1-phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone and 1-phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole 4-ethylthiosemicarbazone, have been synthesized and characterized by MS, IR, ^{1}H NMR spectra and X-ray single crystal diffraction. In solid state, they exhibit reversible photochromic properties under UV light irradiation and heating. Based on the crystal structure, solid IR spectra and theoretical calculation, the photochromic mechanism of the intra- and intermolecular double-proton transfer from the enol form to the keto form is proposed. In solution, stimulated by three chemical inputs (H^+, OH^- and Zn^{2+}), they undergo the deprotonation–protonation and complexation reactions. Based on an absorption band at 355 nm as the output signal, an INHIBIT logic gate combining a NOT and an AND gate has been obtained.

1. Introduction

Organic photochromic compounds have attracted considerable interest because of their potential applications in the fields of high-density data storage, molecular sensors, switches, and information processors *et al.*[1] Lots of work on spiropyrans, spiroxazine, dithienylethenes, fulgides, and Schiff bases have been extensively reported.[2] However, most of them show the reversible photochromic behavior only in the solution state. To develop new compounds with reversible photochromic behavior in the solid state is very important for their applications. Since the first molecular AND logic gate was reported by de Silva and co-workers,[3] molecular systems with photochromic units have been demonstrated to mimic the functions of molecular switches, elementary logic gates and integrated logic gates. New properties can be achieved through the use of a simple molecule upon inputs of different external stimuli, such as light, pH variation, and metal ions. For example, Zhu[4] *et al.* reported spiropyran molecules have the function of AND, INHIBIT, NAND, XOR logic gates and a half-adder in response to UV light, Fe^{3+}, Zn^{2+} and H^+, or a unimolecular half-adder based upon the facile reversible coordination between small molecules and the metal ions Cd^{2+} and Zn^{2+}. Li[5] *et al.* designed an INHIBIT logic gate based on a spiropyran sensitized semiconductor electrode with the variation of photocurrent upon the input signals of 365 nm UV light and >450 nm. Yan[6] *et al.* reported an unsymmetric diarylethene derivative with multiswitched behavior through protonation, coordination and photochemical reactions, and mimic logic functions from an INHIBIT logic gate to a half-subtractor. Jiang[7] *et al.* reported a Schiff base, *N*-3,5-dichloro-salicylidene-(*S*)-*R*-phenyl ethylamine, undergoing reactions of photochemistry, deprotonation, and complexation upon UV stimulation, OH^- and Zn^{2+}. One mono-molecular circuit was obtained, which integrates one OR, two NOT, and four AND gates. So the development of novel mono-molecule system with photo- and chemical switches is becoming an interesting area.

Many thiosemicarbazones derived from 4-acyl pyrazolones with photoisomerization properties have been systemically studied in our laboratory.[8] Although they can offer an enormous structural diversity and tunable photoisomerization properties, they also suffer from a lack of photochromic reversibility in the solid state. In order to overcome the disadvantage, many efforts have been dedicated to design the structure. Finally, the photochromic compound with good reversibility, 1,3-diphenyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone was obtained by the incorporation of 2-ClPh at the 4-position and Ph at the 3-position of pyrazolone.[8e] On the one hand, its derivatives need to be further developed by the structural modification in order to improve the photochromic properties. On the other hand, we

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† Electronic supplementary information (ESI) available: Synthetic procedure for **2**, ^{1}H NMR data of **1–2**, mass spectra of **1–2**, first-order kinetic plots of the photoisomerization reaction of **1** and **2** induced by 365 nm light at room temperature, molecular structure of **II** with atom numberings of **1** and **2**, the crystal data and structure refinement details for **1** and **2**, selected bond lengths (Å) and angles (°), intra- and intermolecular hydrogen bonding geometry in keto form crystal for **1** and **2**, crystal packing in unit cell along the *c* axis for **1** and **2** and the absorption spectra changes under OH^- action; Zn^{2+} action; H^+ action; OH^- and Zn^{2+} actions; OH^- and H^+ actions; Zn^{2+} and H^+ actions; OH^-, Zn^{2+}, and H^+ actions in solution, theoretical calculated details are given. CCDC reference numbers 708004, 708005. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b908326j

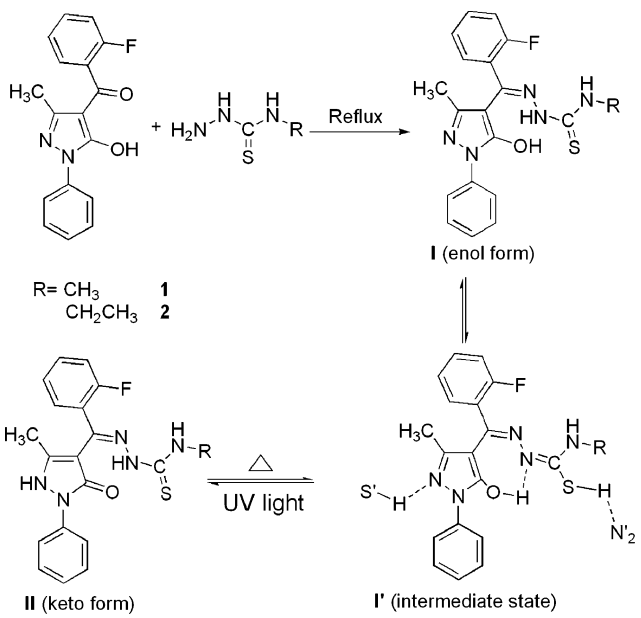
previously studied the photochromic properties of pyrazolone thiosemicarbazones in solid state, but rarely paid attention to the effect of pH on their spectral properties in solution.

In this paper, we introduced the halogen F atom in the 4-position of 1-phenyl-3-methyl-4-benzal-5-hydroxypyrazole 4-methylthiosemicarbazone (PMBP-MTSC)[8b] in order to improve the reversible photochromic ability and the photochromic speed, synthesized two new compounds namely 1-phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone (**1**) and 1-phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole 4-ethylthiosemicarbazone (**2**), which exhibit reversible photochromism in the solid state. By analyses of crystal structure and solid IR spectra, we put forward a photochromic mechanism of the title compounds which is different from the photochromic processes of PMBP-MTSC. At the same time, the molecular logic function of the title compounds in solution was studied by using OH^-, Zn^{2+} and H^+ as inputs and the absorbance value as an output.

2. Results and discussion

2.1 UV absorption and fluorescence spectra in the solid state

Scheme 1 illustrates the synthetic route of the title compounds and their photoisomerization from the white enol form (**I**) to the yellow keto form (**II**). As shown in Fig. 1, it can be observed that new bands appear at 420 nm for **1** and 430 nm for **2** in the UV-Vis absorption spectra of **1** and **2** powders (enol form) irradiated by 365 nm UV light at room temperature, and their intensities increase with irradiation time. Additionally, no change is observed in their UV spectra and decomposition does not occur when these yellow compounds were kept in a dark box for half a year, which indicates that the yellow forms are very stable and retain its coloration memory for a long time. However, the yellow forms (**II**) quickly reverted to the pale yellow (**I**) for **1** at 180 °C and



Scheme 1 Synthetic route and photoisomerization of the title compounds.

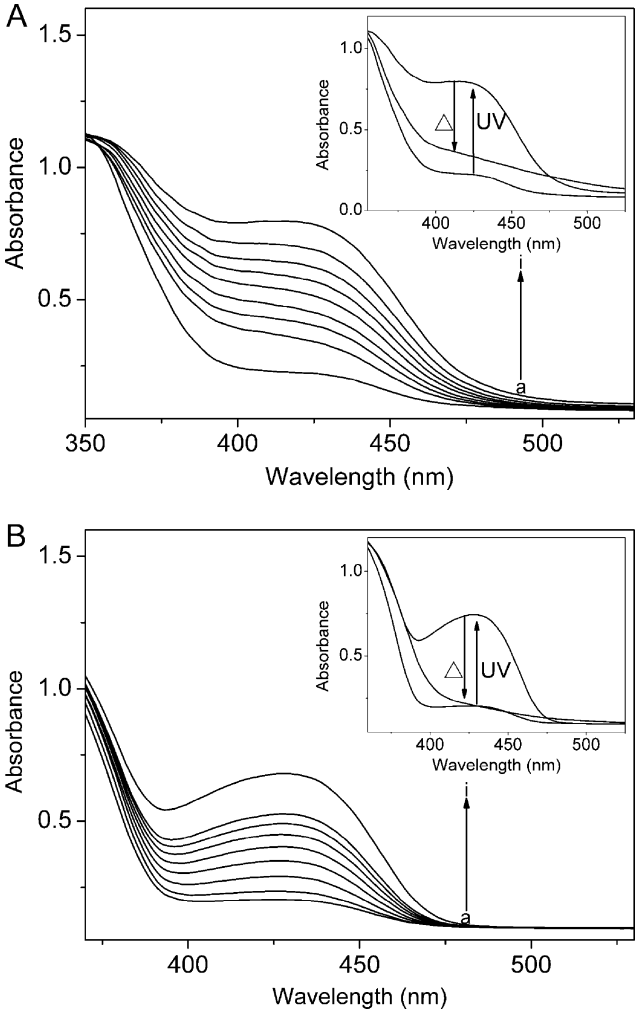


Fig. 1 UV spectra of **1** and **2** powders in the solid state at room temperature. (A) From a to i, each irradiation time (min) for **1** is 0, 4, 8, 12, 20, 30, 48, 72, 150. (B) From a to i, each irradiation time (min) for **2** is 0, 12, 24, 36, 48, 60, 72, 84, 160. Inset: thermobleaching spectra by heating.

the cream for **2** at 195 °C, and the intensity of peaks at 420 and 430 nm gradually decreased. Based on their absorption values, the degree of thermobleaching is *ca.* 79% of **1** and 98% of **2**. Under UV irradiation, the decolored powders return to yellow again. These results suggest that photochromism is reversible.

According to the literature,[9] kinetic rate constants can be determined from the plot of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ against the time (t) (Fig. S4, ESI†). The enol-to-keto isomerization reaction follows well the pseudo-first-order kinetics and the rate constant was obtained from the slope as $k_1 = 3.56 \times 10^{-3}\ s^{-1}$ and $k_2 = 2.17 \times 10^{-4}\ s^{-1}$, respectively. Obviously, the photochromic rate of compound **1** is faster than that of compound **2** due to the smaller steric hindrance of the methyl group than the ethyl group. For the analogue compound 1-phenyl-3-methyl-4-benzal-5-hydroxypyrazole 4-methylthiosemicarbazone,[8b] the kinetic constant of the photoisomerization is $3.91 \times 10^{-4}\ s^{-1}$, which indicates its photoisomerization reaction is slower than that of the compound **1**. The result shows that the electron withdrawing property of the F atom of

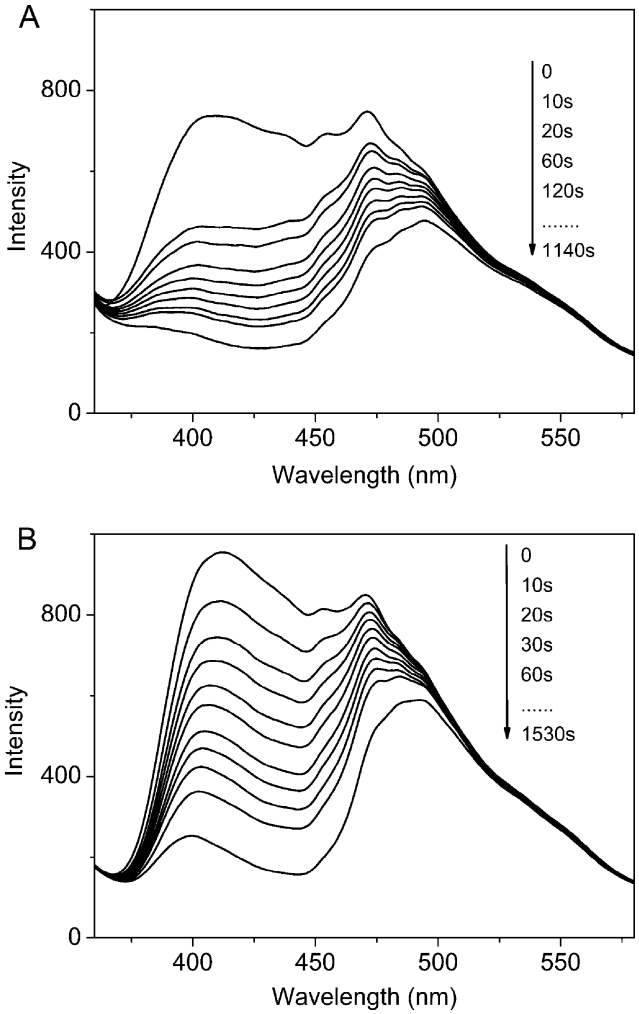


Fig. 2 Fluorescent emission spectra of powders **1** (A) and **2** (B) under 365 nm UV light irradiation at room temperature.

benzyl groups on the 4-position of pyrazole rings increases the photochromic speed.

Fig. 2 is the fluorescent emission spectra of powders **1** and **2** irradiated by 365 nm UV light at different times at room temperature. It can be seen that the emission bands of the white enol form (**I**) for **1** appear at 410 nm and 470 nm after being excited at 310 nm, their intensity gradually decreased with irradiation time, and the emission band at 410 nm finally disappeared. Subsequently, the white enol form (**I**) gradually changes to the yellow keto form (**II**). After heating at 180 °C, the yellow returned to the pale yellow, the emission band at 410 nm appears again, which further indicates that compound **1** has a reversible photochromic property. Similar phenomena are observed in the fluorescent emission spectra of **2** (shown in Fig. 2B). The intensity of the emission bands decreases significantly upon irradiation of 365 nm UV-light due to the formation of the yellow keto form.

2.2 Crystal structure, stability and photochromic mechanism

In order to ascertain the photochromic mechanism, the single crystal structures have been determined. The pale yellow transparent single crystals of **1** and **2** were obtained by slowly evaporating the solution of methanol at room temperature without avoiding sunlight. The molecular structures of **1** and **2**, crystal packing for **1** and **2**, the crystal data and structure refinement details for **1** and **2**, selected bond lengths (Å) and angles (°) and intra- and intermolecular hydrogen bonding geometry in keto form crystals are shown in Fig. S5–S7 and Table S1–S3 (see ESI†). The structures of the two compounds have similar bond length, same space group and unit-cell dimensions. The C7–O1 bond distance is 1.251 or 1.250 Å, which is consistent with the length of the C═O and that of the previously reported analogue compound.[8e] The bond lengths of C–S (1.697 Å for **1** and 1.704 Å for **2**) are also close to the C═S double bond length. It can be deduced that their structures belong to the keto (**II**) form. In solution, we only obtained the keto form crystals. In order to further analyze the stability of the keto and enol forms, theoretical calculations are performed with the GAUSSIAN 03W program package. Taking the total energy of the most stable configuration as a reference, the energy differences (ΔE) of the other isomers obtained in gas phase and in methanol solution are presented in Table S4 (see ESI†). In the gas phase, the calculated ΔE is 0.34 kcal mol^{-1} for **1** (0.27 kcal mol^{-1} for **2**), which indicates the enol form is more stable than the keto one. But the relative energies between the enol and the keto isomers are so small that the interconversion among these isomers easily occurs. In addition, the dipole moment of the keto form (9.28 Debye or 9.22 Debye) is greater than that of the enol form (5.23 Debye or 5.13 Debye). According to the reaction field approach, the polarity increase of the medium should favor a tautomer with greater dipole moment.[10] So in polar media, the energy difference between isomers would be smaller or even that the keto form would become the most stable.[11] The following energy calculation results in methanol solution suggest that the keto form is the most stable isomer, which is in agreement with the experimental fact that the single crystal structures of the title compounds which obtained from the methanol solution are the keto forms.

Hydrogen bond connection diagrams of **1** and **2** are shown in Fig. 3. It can be seen that there is a similar hydrogen bonding configuration in the two crystals, and they are stabilized by intermolecular hydrogen bonds (N2′–H2N′···S, 3.261 Å or 3.206 Å; N5″–H5N″···O′, 2.966 Å or 3.011 Å, the single and double quotation marks represent different molecules) and intramolecular hydrogen bonds (N4′–H4N′···O′, 2.704 Å or 2.712 Å). It is remarkable that the O atom is not only involved in an intermolecular hydrogen bond (N5″–H5N″···O′), but also takes part in an intramolecular hydrogen bond (N4′–H4N′···O′). Moreover, the length of the intramolecular hydrogen bond is obviously shorter than that of the intermolecular one. At the same time, Etter[12] stated that six-membered-ring intramolecular hydrogen bonds take precedence of intermolecular hydrogen bonds. So the proton transfer by the intramolecular hydrogen bond (N4′–H4N′···O′) is much easier than that by the intermolecular hydrogen bond (N5″–H5N″···O′).

Methanol molecules are present in the crystal structure of **1**, which interact with the S atom of the methylthiosemicarbazone moiety, leading to the weak hydrogen bond of O2–H2A···S (3.524 Å, 147°). In the packing arrangement of **1** and **2**, both

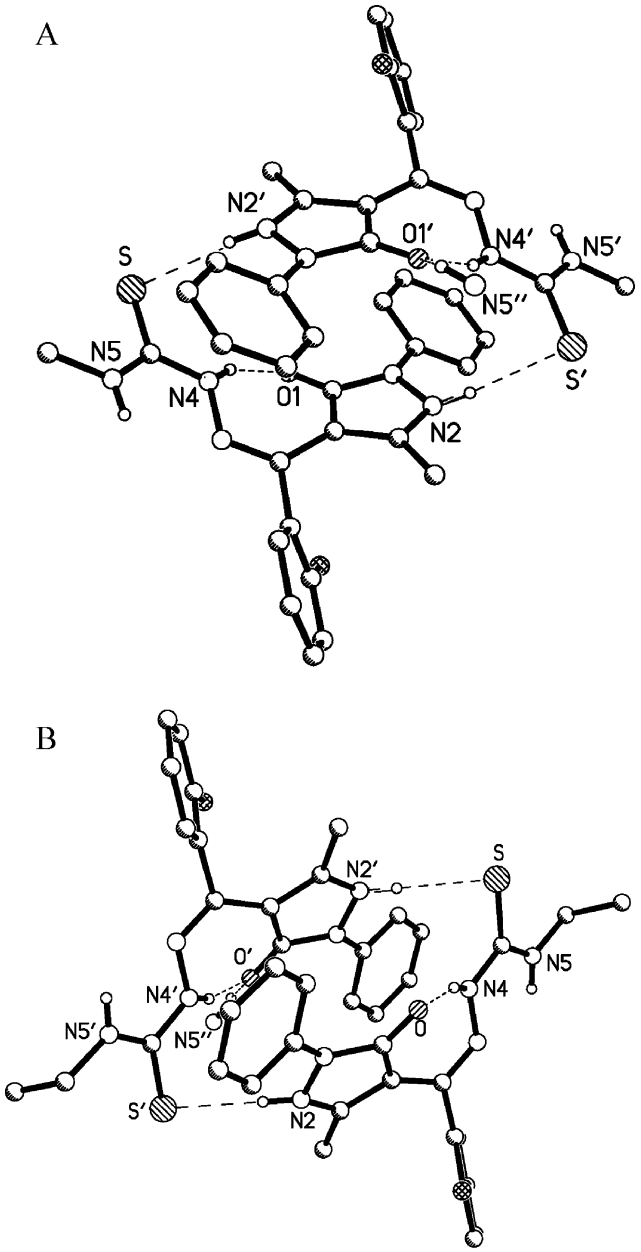


Fig. 3 Hydrogen bond connection diagrams in the molecular structures of **1** (A) and **2** (B) (hydrogen atoms of carbon atoms are omitted, and a prime (′) character in the atom labels are at the equivalent position $(1 - x, 1 - y, 1 - z)$.)

donor and acceptor in these hydrogen bonds are involved in a neighboring molecule, leading the two dimensional network configuration by an antisymmetric way along the *c* axis.

Based on the analysis above, a reasonable photochromic mechanism is proposed. Under UV light irradiation, the intramolecular proton transfers from the O atom to the N4 atom by the channel of N4···H–O. At the same time, the intermolecular proton transfers from the S′ atom to the N2 atom by the channel of N2···H–S′, forming an intermolecular hydrogen bond N2–H···S′. These processes lead to the enol–keto photoisomerization through the intra- and intermolecular double-proton transfer *via* the intermediated (**I′**) as shown in Scheme 1. The photochromic mechanism of the title compounds is different from that of the analogous compound 1-phenyl-3-methyl-4-benzal-5-hydroxypyrazole 4-methylthiosemicarbazone, which is only an intermolecular proton transfer from the O atom of the hydroxyl group to the nitrogen atom on pyrazole ring of the adjoining molecule.[8b]

Numerous attempts have been made to obtain the structures of the colorless single crystals, but we failed because the calculated results indicate the keto form is more stable in polar solution. Solid IR spectroscopy was employed to investigate the configurational changes during the photoisomerization transition. Fig. 4 shows IR spectra of **1** and **2** before and after UV light irradiation at room temperature. Obviously, broad middle vibration bands in the range of 2500–3100 cm^{-1} are observed, characteristic of Schiff bases with a medium strength intramolecular hydrogen bond.[13] This phenomenon is similar to the light-induced hydroxypyrazole derivants[8a,e] and other systems.[14]

However, upon irradiation with UV light, new sharp bands appear at 1671 cm^{-1} for **1** and 1664 cm^{-1} for **2**, respectively, which are attributed to C═O stretching vibrations. It is

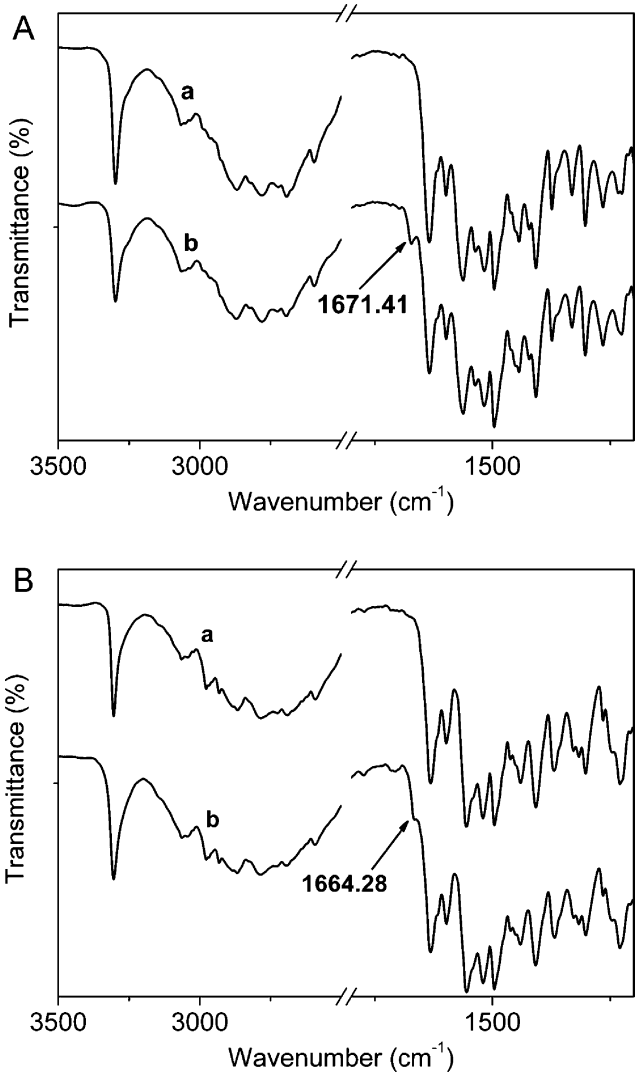
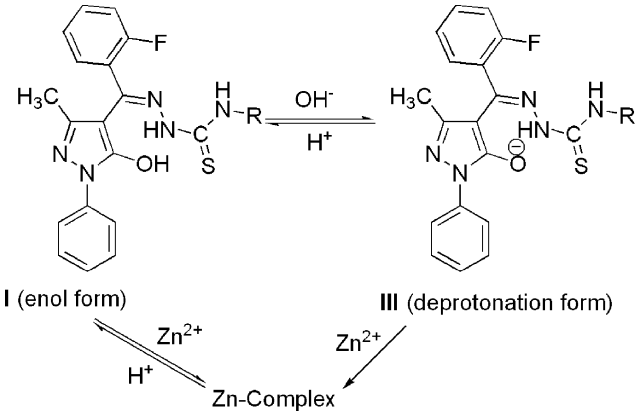


Fig. 4 IR spectra of **1** and **2** before (a) and after (b) 365 nm UV light irradiation.

similar to the analogous compound reported previously,[8e] The results indicate that configurational transformation between the enol form and the keto form is in agreement with the analysis of the crystal structure above.

2.3 Absorption spectral changes stimulated by three inputs in solution

We previously focused on the photochromic properties and complexation behaviours of pyrazolone thiosemicarbazones, but rarely paid attention to the effect of pH on the spectral properties of these kind of compounds in solution. Actually, the compounds **1** and **2** are quite sensitive to acid and base. When aqueous NaOH (0.1 M) is added into the system, a deprotonation reaction takes place immediately. So we selected OH^- as the first input signal. As shown in Fig. 5, the absorption bands at 320 nm gradually decrease and red shift as the pH value increase. At the same time, the new absorption bands attributed to the deprotonated products (**III** in Scheme 2) appear at 344 nm for **1** and 261, 345 nm for **2**, respectively. But the changes are not obvious when the pH value is above 7.04 for **1** (7.94 for **2**). Moreover, there are isosbestic points at 336 nm for **1** and 289, 338 nm for **2**, respectively.



Scheme 2 Transitions among deprotonation, protonation and coordination reactions.

Pyrazolones are an important class of ligands in coordination chemistry and have been extensively studied for selectivity and sensitivity towards various metal ions.[15] Zinc complexes often

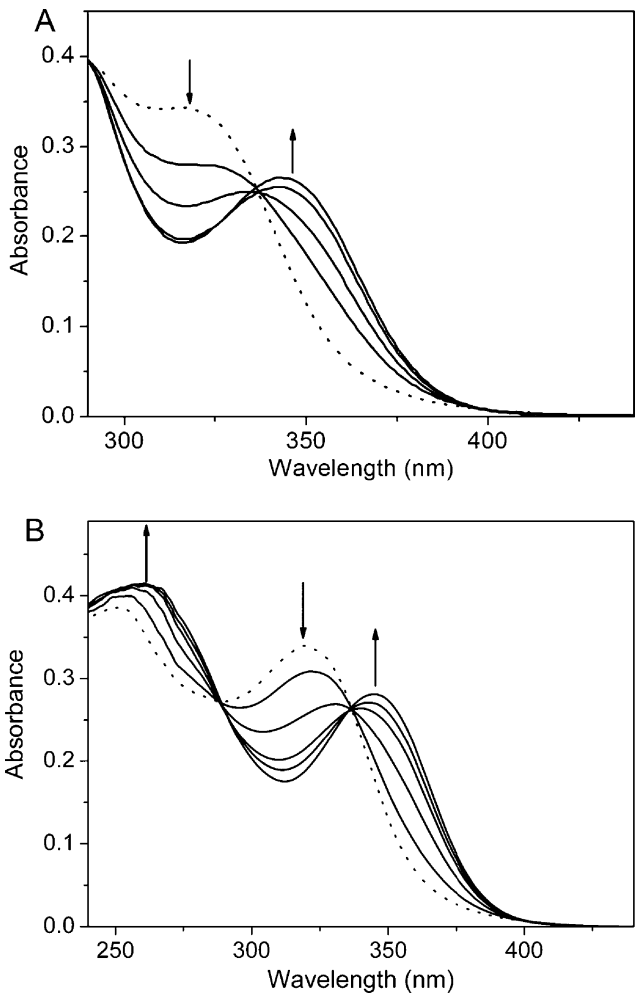


Fig. 5 Absorption spectra of compounds **1** (A) and **2** (B) in methanol solution (2×10^{-5} mol L^{-1}) before (dashed line) and after (solid line) titration with the 0.1 M NaOH aqueous. (A) pH values are 4.74, 5.14, 5.62, 6.93, 7.04, respectively. (B) pH values are 4.56, 5.04, 5.47, 6.95, 7.41, 7.94, respectively.

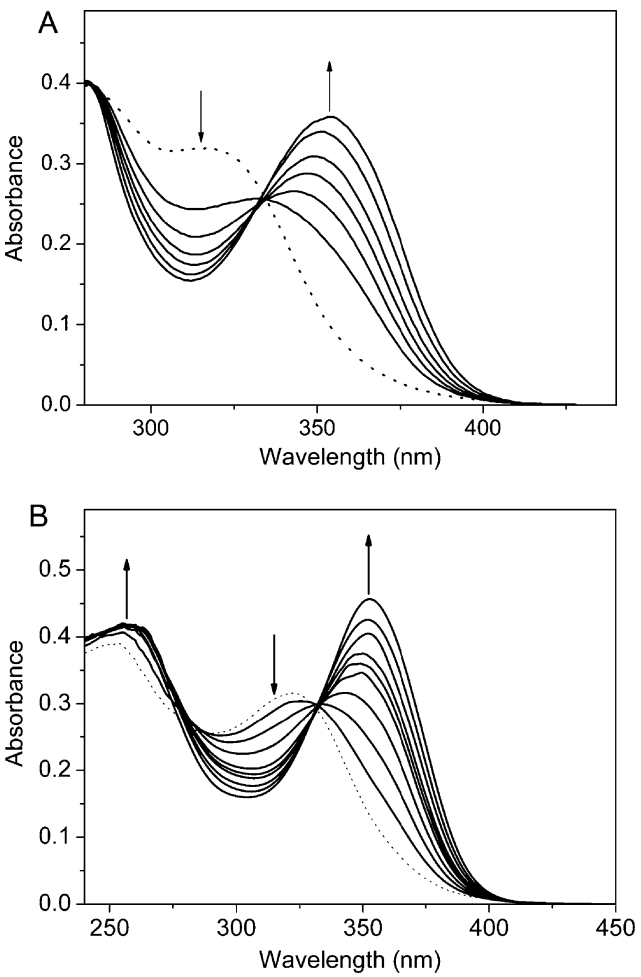


Fig. 6 UV-vis absorption spectra of 1 (A) and 2 (B) in methanol solution (2×10^{-5} mol L^{-1}) with continuous titration by the $ZnCl_2$ solution (0.1 M).

display strong spectral changes, which can be used as a detectable output signal for molecular devices. So we introduced the Zn^{2+} ion as the second input signal. The coordination reaction takes place as soon as the $ZnCl_2$ solution (0.1 M) is added into the methanol solution of **1** or **2**, leading to obvious changes in the absorption spectra, as shown in Fig. 6. For compound **1**, it can be seen that the intensity of the original peak around 320 nm (dashed line) gradually decreases with Zn^{2+} titration, but the new peak at the 355 nm appears due to the formation of the Zn-complex. Similar phenomena were also observed from the UV-vis absorption spectra of compound **2**. However, there are some differences on spectra changes in the range of 235–275 nm. It may be due to the substituent effect of methyl group or ethyl group on the side-chain of thiosemicarbazone. Compared with the absorption spectra of the ligands, that of the complexes take on the red-shift phenomenon due to metal perturbed intra-ligand $\pi \rightarrow \pi^*$ transition.

Then the cooperated actions of two inputs are studied. As shown in Fig. 7 (curves a to b), the typical absorption bands at 344 nm and 345 nm appear after the methanol solutions of **1** and **2** were titrated with the NaOH aqueous, which indicates that the ligands **1** and **2** are deprotonated, and transformed to (**III**) in Scheme 2. Then by titrating the deprotonated form (**III**) with the $ZnCl_2$ solution, the absorption bands at 344 nm and 345 nm red shifted to 355 nm (curves b to c), which is attributed to the bands of the zinc complexes mentioned above. So we can also obtain the zinc complex after the two-step process.

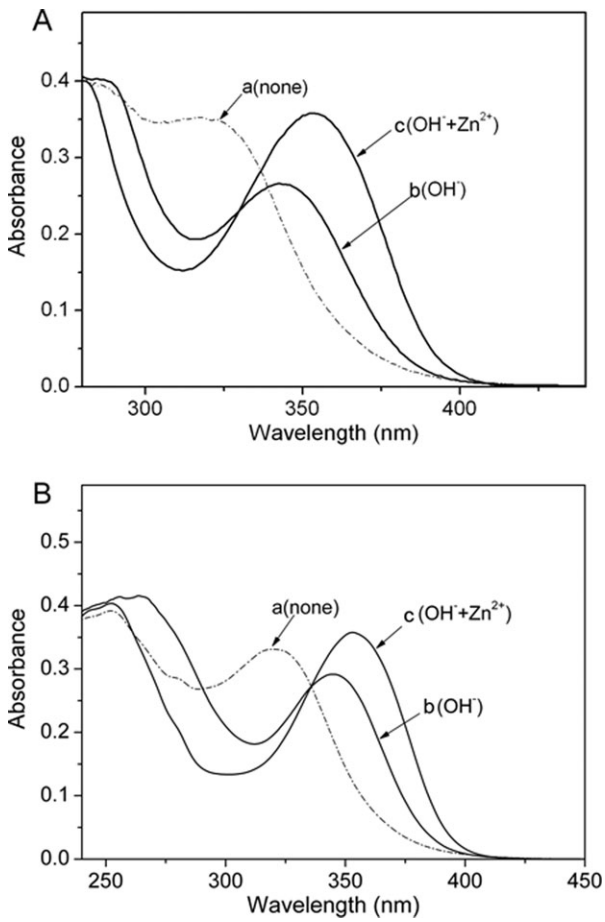


Fig. 7 Absorption spectra of compounds **1**(A) and **2**(B) titrated by the NaOH (0.1 M) and the $ZnCl_2$ solution (0.1 M).

Finally, we choose H^+ as the third input signal. First, by titrating **1** and **2** with aqueous NaOH, we get the deprotonated product (**III**). Then titrating deprotonated products continuously with hydrochloric acid (0.1 M) produces spectral changes (Fig. 8). In the case of compound **1**, the absorption band at 344 nm decreases, while the new band at 320 nm appears with the addition of hydrochloric acid, finally recovering the original spectral shape, as depicted in Fig. 8A. Similar phenomona also are observed for compound **2** in Fig. 8B. When the protonated form (**I**) in acidic methanol solution is continuously added the base solution, it returns to the deprotonated form. This circle can be repeated for many times, which shows that the deprotonated-protonated process of compounds **1** and **2** is reversible. Under the alternating action of base and acid, it can perform the reversible process as a pH switch through

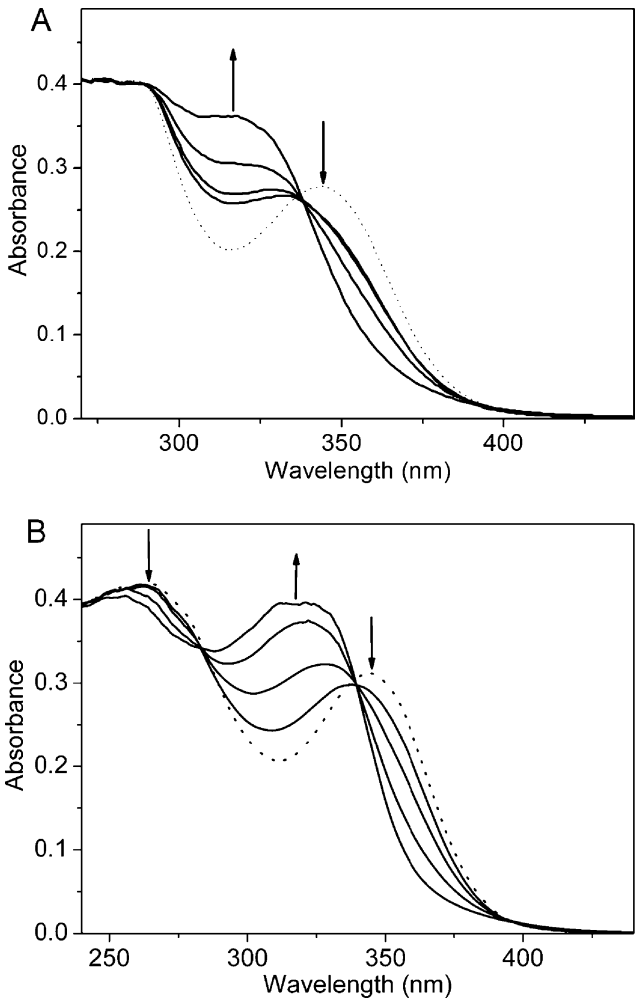


Fig. 8 (A) Absorption spectra of **1**-(**III**) (dashed line, deprotonated form) and after continuous titration with H^+ (solid line, protonated form), pH values are 7.04, 6.28, 5.88, 4.97, 3.98, respectively; (B) Absorption spectra of **2**-(**III**) (dashed line, deprotonated form) and after continuous titration with H^+ (solid line, protonated form). pH values are 7.94, 6.28, 5.07, 4.42, 3.80, respectively.

isosbestic point, which indicates that the acid–base equilibrium occurs between the deprotonated and protonated species of **1** and **2**, respectively.

No color change could be detected by the naked eye on addition of the acid or the base. However, a blue shift can be observed with dropwise addition of hydrochloric acid to the basic methanol solution of **1** and **2** from Fig. 8. With the pH value decreasing from 7.04 to 3.98 for compound **1** and from 7.94 to 3.80 for **2**, the maximum absorption band moves hypsochromically by 344 nm to 320 nm and 345 nm to 320 nm, respectively.

As mentioned above, when compounds **1** and **2** are titrated with the $ZnCl_2$ solution, the complexes are formed. Then we utilize hydrochloric acid to titrate these complexes. As shown in Fig. 9, the intensity of the absorption bands at 355 nm decreases gradually and blue shifts to 334 nm when titrating with excessive hydrochloric acid, which indicates that the zinc complexes can decompose under acidic conditions.

Subsequently, we introduce the three inputs to **1** and **2** one by one. For the title compounds, the absorption spectra changes under OH^- action, Zn^{2+} action, H^+ action, OH^- and Zn^{2+} actions, OH^- and H^+ actions, Zn^{2+} and H^+ actions, OH^-, Zn^{2+}, and H^+ actions, are illustrated in the ESI (Fig. S8–S11†), respectively. Among all of the stimulations, only the Zn^{2+} action and the OH^- plus Zn^{2+} actions can induce a strong absorption at 355 nm due to the formation of the zinc complexes. Fig. 10 presents the final absorbance intensity at 355 nm of title compounds at all possible actions relating to the three inputs. In summary, under the individual actions of the OH^-, Zn^{2+}, and H^+ as well as the combination of these, **1** and **2** can accomplish the reactions of deprotonation, complexation, and protonation producing obvious optical outputs: a UV-vis absorption band at 355 nm.

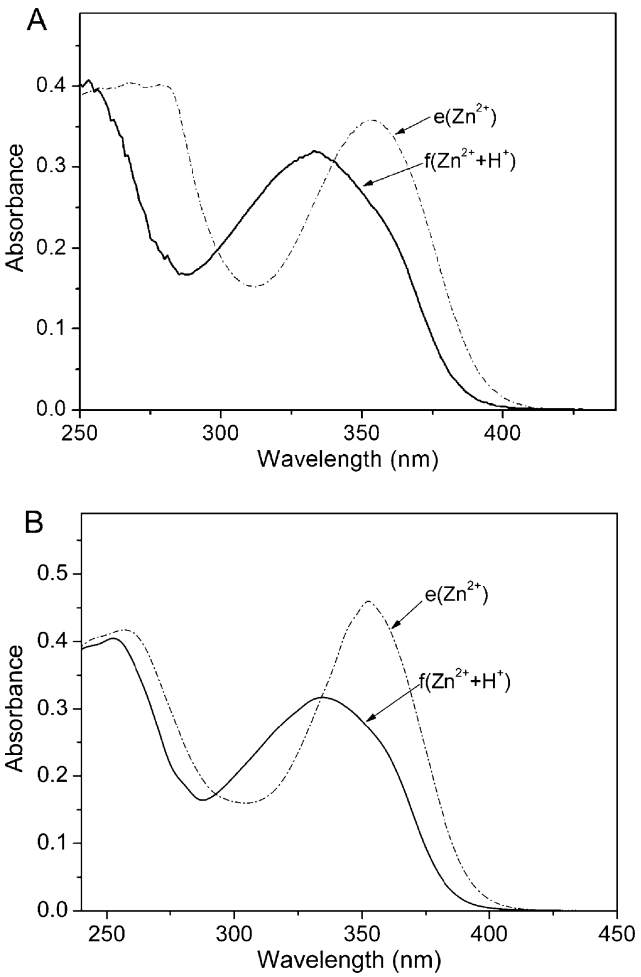


Fig. 9 Absorption spectra of the zinc-complex corresponding to **1** (A) and **2** (B) (dashed line) and after titrating with excessive hydrochloric acid (0.1 M) (curves e to f).

2.4 INHIBIT logic function

The communication between the input signals, OH^- (IN1), Zn^{2+} (IN2), and H^+ (IN3) and the output signals, the absorbance value at 355 nm (OUT), can be described with the binary logic. The absence of inputs (OH^-, Zn^{2+}, and H^+) or output values (absorption) below a predefined threshold

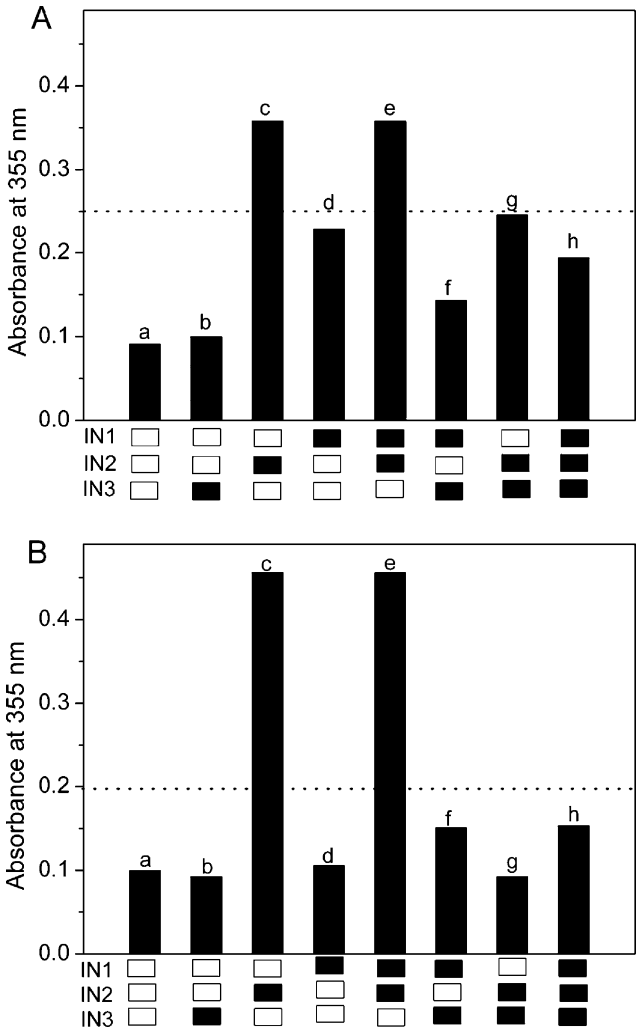


Fig. 10 Under the stimulation of OH^- (0.1 M, IN1), Zn^{2+} (IN2), and H^+ (0.1 M, IN3) (IN1, IN2, IN3 in the string of a: 0 0 0; b: 0 0 1; c: 0 1 0; d: 0 1 1; e: 1 0 0; f: 1 0 1; g: 1 1 0; h: 1 1 1), (A) the changes of absorbance intensity at 355 nm of **1**; (B) the changes of absorbance intensity at 355 nm of **2**. (□ represents inputs that are 0, ■ represents inputs that are 1).

Table 1 Truth table for the INH logic gate

Input		Output (at 355 nm)		
OH^-	Zn^{2+}	H^+	**1**	**2**
0	0	0	0	0
0	0	1	0	0
0	1	0	1	1
0	1	1	0	0
1	0	0	0	0
1	0	1	0	0
1	1	0	1	1
1	1	1	0	0

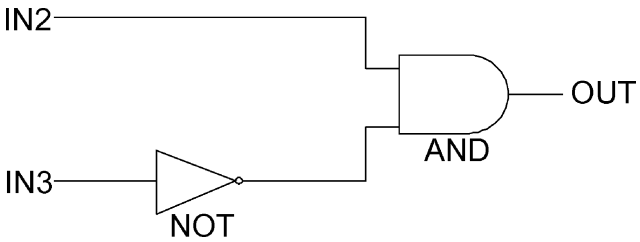


Fig. 11 INHIBIT Logic circuit of compound **1** and **2** with inputs.

level (absorbance value of 0.3) are translated into binary "0", while the presence of an input or outputs above the threshold corresponds to binary "1", in accordance with the positive logic convention. For example, the input string 0 0 0 indicates that the three stimulation inputs are off. Under these conditions, the absorbance at 355 nm is low. The output string is 0. Instead, the input string 1 1 0 indicates that the OH^- and Zn^{2+} are on. Under these conditions, the zinc complex is the dominant product. The output string is 1. Following similar consideration, the eight output strings corresponding to the eight possible combinations of input strings can be determined. From the spectral investigations illustrated above, the absorption band at 355 nm (OUT) can be achieved in two situations: one is by directly titrating with the $ZnCl_2$ solution, the other one is by titrating the deprotonated form with Zn^{2+}. In other words, only when IN1 = 0, IN2 = 1, and IN3 = 0 or IN1 = 1, IN2 = 1, and IN3 = 0, the output signal (OUT) is 1.

According to the two histograms (Fig. 10), the truth table (Table 1) can be obtained. From which, we can see that this chemical system responds to an input string of three binary digits (IN1, IN2, IN3) producing an output string of one binary digits (OUT). Consequently, the logic behavior of the molecular switch corresponds to an INHIBIT logic gate by combining a NOT and an AND gate (Fig. 11).

3. Conclusion

Two novel pyrazolone thiosemicabazone derivatives which exhibit reversible photochromic properties in the solid state are synthesized. The analyses of crystal structures and IR spectra suggest that the photochromic mechanism is the intra- and intermolecular double-proton transfer *via* hydrogen bonds, accompanied by the isomerization between the enol form (**I**) and the keto form (**II**). This is further confirmed by theoretical calculations. In solution, the interplay of the three stimulated inputs and one optical output can be exploited to implement logic operation at the molecular level. Indeed, the logic function executed by this particular molecular switch is equivalent to an INHIBIT logic circuit incorporating a NOT and an AND gate. This contribution not only develops a multi-switch single molecular logic circuit but also presents a potential candidate for future high-density optical storage devices.

4. Experimental section

4.1 Instrumentation

Melting point was measured with a TECH X-6 melting point apparatus and was uncorrected. The IR spectra were recorded on a BRUKER EQUINOX-55 Spectrometer, and ^{1}H NMR experiments were carried on an INOVA-400 ^{1}H NMR Spectrometer in DMSO-d_6. Mass spectra were determined with HP1100 LC-MS. The absorption spectra were measured using Hitachi U-3010 spectrophotometer. A 15 W lamp in ZF-8 Ultraviolet Analysis Instrument was used as the light source for photocoloration and the distance between the sample and light source was 15 cm. Solutions for UV-vis absorption spectra were titrated directly in 1 cm absorption cells by successive additions of corresponding chemical reagent using a microlitre syringe. All of the spectral analyses were accomplished in methanol. The solution concentrations of **1** and **2** for spectral analysis was 2.0×10^{-5} M. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer (A 100 W Xenon lamp as light source), and the breadths of excitation and emission slits were both 5.0 nm. All measurements were performed at ambient temperature.

4.2 Materials

4-Ethyl-3-thiosemicarbazide and 4-methyl-3-thiosemicarbazide were purchased from the Aldrich Company, USA. 1-Phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole (**PM2FHP**) was synthesized according to the literature with a minor modification.[16] (Yield: 88.76%; m.p. 118.6–120.1 °C). All other reagents were AR. grade and purchased from commercial suppliers, and used without further purification.

4.3 Synthesis of compound 1

1-Phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone was prepared by mixing **PM2FHP** (5 mmol) and 4-methyl-3-thiosemicarbazide (5 mmol) in 30 ml of methanol in the presence of glacial acetic acid (1 ml) at 70 °C for *ca.* 4 h under magnetic stirring. After cooling down to room temperature in the dark, white powders were obtained in a 73.49% yield. m.p. 219.7–220.9 °C. The spectroscopic data are as follows. IR (ν cm^{-1}): (a) the white powder before irradiation: 3298 ν(N–H), 3066–2596 ν(O–H), 1630 ν(C=N), 1561, 1496 ν(phenyl), 1408, 1374 ν(pyrazolone-ring), 1303 ν(C=S). (b) the yellow powder after irradiation: 3298 ν(N–H), 3066–2596 ν(O–H), 1671 ν(C=O), 1630 ν(C=N), 1561, 1496 ν(phenyl), 1408, 1374 ν(pyrazolone–ring), 1303 ν(C=S). MS: [M + 1] = 384.1 ($C_{19}H_{18}N_5OSF$ formula weight: 383.44). ^{1}H NMR (DMSO-d_6) (δ, ppm): 1.651 (3H, N5–CH_3), 3.013–3.002 (3H, Pz–CH_3), 7.454–7.174 (5H, Ph),

7.778–7.507 (5H, C_6H_4F + N4–H), 7.912 (1H, N5–H), 8.233 (1H, Pz–NH).

Compound **2** was prepared in a very similar way. Experimental details and spectroscopic information can be found in the ESI.† The synthesis routine of **1** and **2** is presented in Scheme 1.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 20762010 and 20866009), Scientific Research Program of the Higher Education Institution of XinJiang (XJEDU2006I04 and XJEDU2008S08), the Key Project of Ministry of Education (209138) and the Project of "Western light" of Chinese Academy of Science.

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