

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Fluorescence Modulation of a Pyrazolones Dye in the Solid State Based on Energy Transfer

Hu Liu, Ji-Xi Guo, Dian-Zeng Jia*, Ming-Xi Guo, Lang Liu, Dong-Ling Wu

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

New pyrazolones dye is synthesized and its fluorescence modulation is achieved based on energy transfer. The prepared pyrazolones dye is combined with photochromic pyrazolones to obtain fluorescence photoswitching material (FPM), which exhibits stable and reversible fluorescence photoswitching property in the solid state. Upon characterization of the samples by ^1H NMR spectra, XRD, FT-IR, UV spectrum and fluorescence spectrum, it was found that photochromic pyrazolones and pyrazolones dye integrally retained the inherent properties in the FPM, respectively. An investigation of FPM revealed that the photoswitching response depended on fluorescence dye species, the content of fluorescence dye and the synthetic route of FPM. The photoswitching mechanism of FPM was studied in detail by FT-IR, UV spectrum and fluorescence spectrum techniques. The results show that the photochromism of photochromic pyrazolones plays an important role in the efficient energy transfer from pyrazolones dye to keto-form photochromic pyrazolones. The emission wavelength of the pyrazolones dye hardly induces the photochemical reaction of photochromic pyrazolones in FPM, which has potential to be used as non-destructive fluorescence readout of optical information. This study represents a simple and efficient alternative to the covalent system to obtain FPM, and it may be applied in photoelectronic devices.

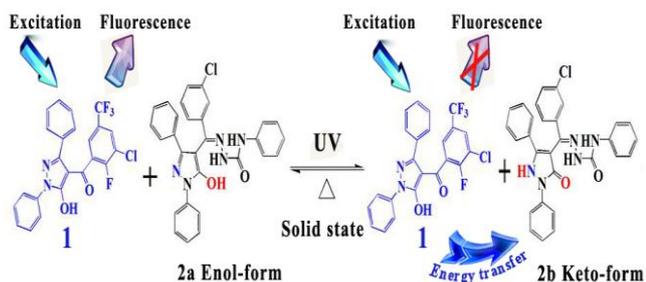
1. Introduction

Due to the non-invasive character, high selectivity and high sensitivity of fluorescence detection, coupling fluorescence molecule to photochromic units¹⁻⁴ and doping fluorescence dye into photochromic system⁵⁻⁸ are two attractive ways to develop multifunctional FPM for optical memories,⁹⁻¹¹ super resolution imaging,^{12,13} and protein trafficking in living cells.¹⁴⁻¹⁶ To realize fluorescence photoswitching, i.e., to modulate fluorescence emission upon external light stimulus, photochemical reaction is commonly the fundamental regulatory step. Photochromism, a photoinduced reversible reaction between two isomers, is one of the essentially photochemical reactions to facilitate the reversible fluorescence photoswitching process in FPM.^{17,18} Various reports have been published regarding reversibly photoswitchable fluorescent molecules in recent years. Photochromic molecules, such as diarylethene, spiropyran or azobenzene, are employed as key units to toggle the fluorescence “on” and “off” repeatedly.^{19,21} For instance, Liao et al. constructed a photoswitchable

nanoparticles by grafting the fluorescent carbon nanoparticles with the copolymers of styrene and spiropyran, the fluorescent of fluorescent carbon nanoparticles was modulated by the copolymers of styrene and spiropyran.²² Diaz et al. devised skillfully a photoswitchable semiconductor nanocrystals based on energy transfer between the semiconductor core functions and multiple photochromic diheteroarylethene groups.²³ However, among the photomodulatable compounds mentioned above, they only show photoreaction property in solution, which limit their applications in photoelectronic devices. In the large family of photochromic material, the photochromic pyrazolones material can exhibit excellent fatigue resistance, good thermal stability in pure solid state. Therefore further works, which utilize photochromic pyrazolones to modulate the fluorescent of fluorescence dye, can exploit the excellent properties of photochromic pyrazolones.^{24,18} We have successfully developed the reversible fluorescence photoswitching system based on doping inorganic fluorescence dye ($\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$) into photochromic pyrazolones.²⁵ But there is differences in physical

and chemical properties between inorganic fluorescence dye and photochromic pyrazolones in this material, which may limit this material to be applied in photoelectronic devices. Thus, utilizing the similar structure of pyrazolones dye and photochromic pyrazolones, we conceive another FPM by doping pyrazolones dye into photochromic pyrazolones system.

Fortunately, the as-synthesized pyrazolones dye shows strong fluorescence emission and optical waveguide performance in the solid state. So the developed FPM can be exploited for photoswitches and optical waveguide devices.^{26,27} In this work, we report a simple FPM in which pyrazolones dye is blended with photochromic pyrazolones: 1,3-diphenyl-4-(3-chlorobenzal)-5-hydroxypyrazole-4-phenylsemicarbazone (**2a**) as the photochromic compound and 1,3-diphenyl-4-(3-chloro-2-fluoro-5-trifluoromethyl)-5-pyrazolone (**1**) as the fluorescence dye. The constructed FPM shows high efficiency and remarkable fatigue-resistance in the solid state. Schematic illustration of this photoswitchable system is shown in Scheme 1.



Scheme 1 Schematic illustration of energy transfer of FPM. After 365 nm light irradiation, the fluorescence of **1** is quenched due to intermolecular energy transfer from **1** to **2b**.

The photochromic pyrazolone molecule is a modulator as an energy acceptor of **1** to toggle fluorescence “on” and “off” following with 365 nm light irradiation or heating. We choose **1** as a desirable compound to realize fluorescent toggling by photochromic pyrazolones as photomodulator because of the fluorescent emission band of **1** overlaps well with the absorption spectrum of the keto-form isomer of photochromic pyrazolone unit. This is an essential criterion for effective energy transfer between the keto-form isomer of photochromic pyrazolone and **1**. In this case, the photoinduced switching of photochromic pyrazolone unit converts from enol-form isomer to keto-form isomer, which efficiently modulate the ON/OFF switching of fluorescence emission of **1**. Such an observation may provide an alternate approach for designing and developing novel optoelectronic materials.

2. Experimental

2.1 Materials

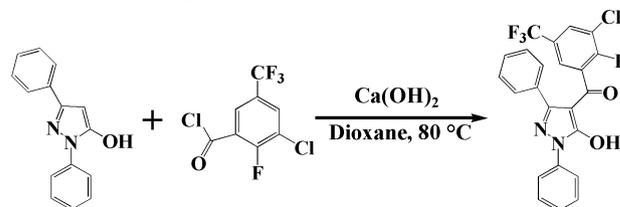
1,3-Diphenyl-5-pyrazolone (DPP) was synthesized according to the literatures.²⁸ 4-phenylsemicarbazide (PSC), 3-chlorobenzoyl chloride and 3-chloro-2-fluoro-5-trifluoromethyl)-benzoyl chloride were purchased from Aldrich Company USA. The other materials were AR grade obtained from commercial sources and used without further purification.

2.2 Instrument

¹H NMR spectra were performed on an INOVA-400 NMR spectrometer with DMSO-*d*₆ as solvent. Melting point was measured with a TECHXT-5 melting point apparatus. The elemental analysis were made on FLASH EA 1112 Series NCHS-O analyser. Absorption spectra were measured on Hitachi UV-3010 spectrometer equipped with an integrating sphere accessory. Fluorescence spectra were studied using a Hitachi F-4500 fluorescence spectrophotometer (an optical filter was used at the excitation window). FT-IR spectra were recorded by using infrared diffuse reflectance spectroscopy in the range 400–4000 cm⁻¹ on a BRUKER EQUINOX-55 spectrometer. A ZF-1 ultraviolet analysis instrument equipped with an ultraviolet lamp (15 W cm⁻²) as the light source was used to induce photochromic reactions, the distance between the sample and the light source was 15 cm.

2.3 Synthesis

2.3.1 Synthesis of pyrazolones dye



Scheme 2 Synthesis route of **1**.

The intermediate 1,3-diphenyl-4-(3-chlorobenzal)-5-pyrazolone (DP3CIBP) and 1,3-diphenyl-4-(3-chloro-2-fluoro-5-trifluoromethyl)-5-pyrazolone (**1**) were synthesized according to literature (Scheme 2).²⁴ For **1**. Yield: 78%. Mp. 193.5-194.7 °C. MS: *m/z*M+: 460.1. Elemental analysis: (C₂₃H₁₃ClF₄N₂O₂): Calcd. (%) C, 59.95; H, 2.84; N, 6.08. Found: (%) C, 59.65; H, 2.91; N, 6.12. ¹H NMR (400 MHz, DMSO-*d*₆): 8.80-8.75 (m, 1H), 8.57 (Substituted phenyl-ring, 2H), 8.47-6.92 (phenyl-ring, 10H).

FT-IR (ν , cm^{-1}): 3082 $\nu(\text{O-H})$, 1673 $\nu(\text{C=O})$, 1595, 1534 $\nu(\text{phenyl})$, 1494, 1443 $\nu(\text{pyrazole-ring})$, 1250, 1050 $\nu(\text{C-O})$.

2.3.2 Synthesis of photochromic pyrazolones compound

1,3-Diphenyl-4-(3-chlorobenzal)-5-hydroxypyrazole-4-phenyl-5 semicarbazone (**2a**) was synthesized according to the literature.²⁵

2.3.3 Synthesis of FPM

Several methods have been used to fabricate FPM: 1) When photochromic pyrazolones is dissolved by the polar solvents, the photochromic property of photochromic pyrazolones is easily affected by solvation during the drying process. The constructed FPM can't exhibit reversible or even no photochromic property (Fig. S2(C, D)), which is crucial for fluorescence modulation. Unfortunately, there is not a suitable solvent which can allow photochromic pyrazolones occur reversible photoisomerization reaction in the solution. 2) After optimizing the experiment conditions, the co-crystallization of **1** and **2a** is a more suitable method. Therefore, we designed and constructed successfully FPM during the synthesis process of **2a** by adding the compound **1** according to the literature of our previous work.²⁵ After the reaction and then cooling down to room temperature, white powders were obtained from the solution and repeatedly purified by ethanol at room temperature. The purified powders were directly used for spectroscopic analyses. Different proportion of FPM was successfully prepared by this way. Especially proposed, **1** can not react with 4-phenylsemicarbazide for its steric hindrance effect, so FPM is only composed of **1** and **2a**, which was confirmed by XRD data (Fig. S1A). The concentration of **1** in FPM was calculated by ^1H NMR data (Fig. S1(B-F)).

3. Results and Discussion

3.1 Basic properties of the photochromic pyrazolones and pyrazolones dye

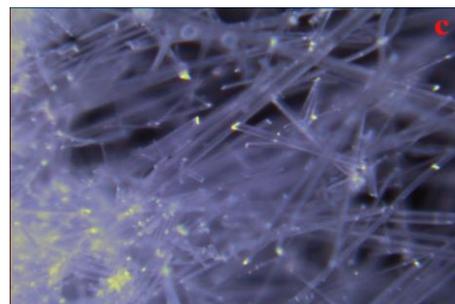
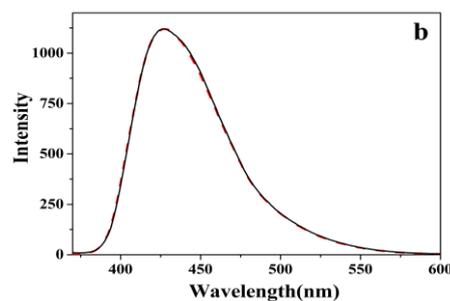
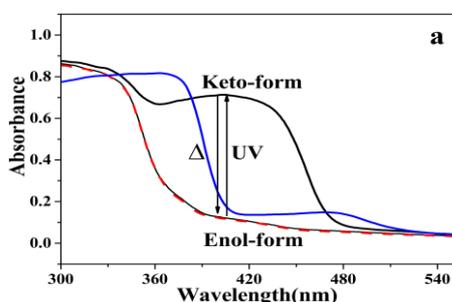


Fig. 1 (a) Absorption spectra changes of **2a** under 365 nm light irradiation (black line) and heating (red dash line), absorption spectra of **1** (blue line) in the solid state. (b) Fluorescence emission spectra of **1**, before (red dash line) and after (black line) 365 nm light irradiation for 60 minutes in the solid state ($\lambda_{\text{ex}} = 330$ nm). (c) Fluorescence image of **1**.

The absorption spectra of **2** and **1** were measured in the solid state, respectively (Fig. 1a). The **2a** transfers into **2b** (photoisomerization product of **2a**) with 365 nm light irradiation, and the absorption band intensity (350-470 nm) of **2b** is increasing by photoisomerization of **2a**. The original absorption spectrum of **2a** is recovered completely by heating at 120 °C in a constant temperature oven. There was almost no absorption for **1** after 400 nm, which excludes the possibility of self absorption. In addition, the fluorescence spectral of **1** is not affected by 365 nm light irradiation, which indicates that **1** is photostable under 365 nm light irradiation (Fig. 1b). The fluorescence emission spectrum of **1** centered at 417 nm ($\lambda_{\text{ex}} = 330$ nm) and the fluorescence image of **1** (Fig. 1c) show that **1** has intense fluorescence. As shown in Fig. 1c, the microtopography of **1** is the rod-like structure, there are two luminescent spots in the two endpoints of each rod, which indicates that **1** is an optical waveguide material in pyrazolone derivatives. So developing FPM may be helpful to exploit the application value of pyrazolones dye and photochromic pyrazolones in photoelectronic devices.

3.2 IR spectrum of FPM

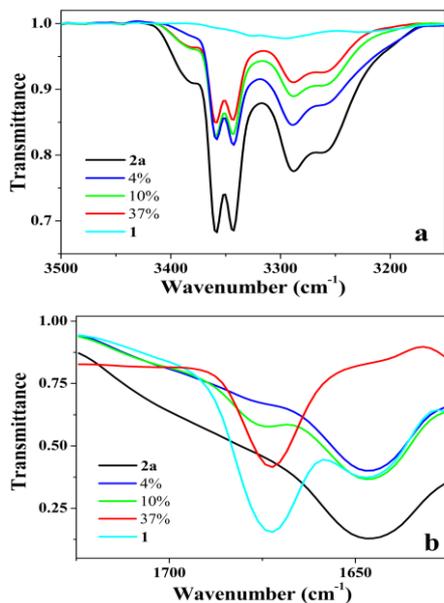


Fig. 2 (a) IR spectra of pure **2a**, FPM (the concentration of **1**: 37 wt%, 10 wt% and 4 wt%), and pure **1** range from 3150 cm^{-1} to 3500 cm^{-1} , and (b) range from 1625 cm^{-1} to 1725 cm^{-1} in the solid state, respectively.

The useful IR spectra are employed to confirm that FPM is composed of **1** and **2a** (Fig. 2). As shown in Fig. 2a, broad absorption bands of **2a** in the range of 3000-3500 cm^{-1} are observed, which suggests that there exist characteristic of Schiff bases with a medium strength intramolecular hydrogen bond in the solid state.²⁹ Obviously, broad absorption bands of **2a** are also observed in FPM, the result confirms that **2a** is one of components of FPM. The absorption band of 1673 cm^{-1} can be ascribed to C=O vibration of **1** in Fig. 2b, with increasing concentration of **1**. The intensity of absorption band at 1673 cm^{-1} increases markedly, which distinctly demonstrates that **1** is one of components of FPM. So FPM is composed of **1** and **2a**. Other peaks of IR spectra were identified in the experiment section.

3.3 Photoswitching mechanism of FPM

The helpful FT-IR spectroscopy is used to explain the photoswitching mechanism of FPM. As shown in Fig. S3A, a new sharp peak appears at 3400 cm^{-1} after **2a** is irradiated by 365 nm light (curve for b), attributed to the N-H stretching vibration in the pyrazole-ring.¹⁸ In addition, a same phenomenon appears in the FPM, the result indicates that the photoisomerization from **2a** (enol-form) to **2b** (keto-form) occurs during 365 nm light continuous irradiation in the FPM (Fig. S3(B-D)).

The colour of **2a** reversibly changed from white to yellow. For FPM, same method was used to evaluate photochromic property

of FPM. When irradiated by 365 nm light, the colour of FPM changed from white to yellow, the opposite process occurred when FPM was heated at 120 $^{\circ}\text{C}$ for ten minutes. This result assuredly demonstrated that FPM indeed showed photochromic property (Fig. S4).

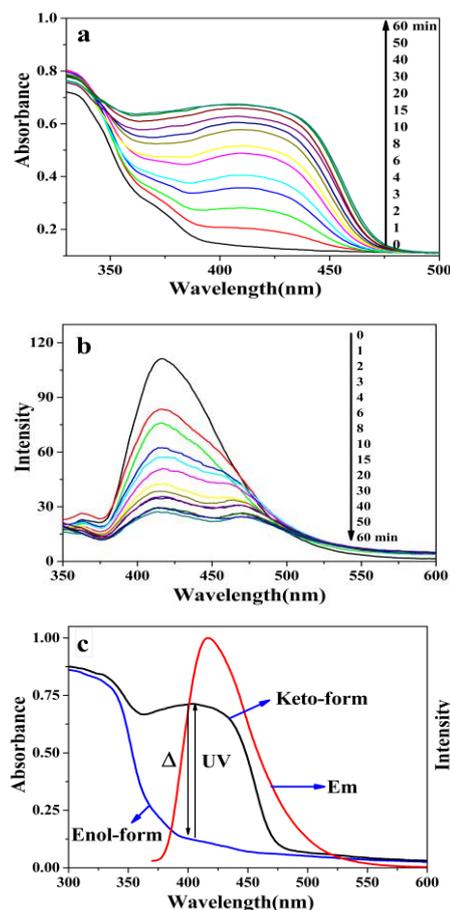


Fig. 3 (a) and (b) Absorption spectra and fluorescence emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) changes of FPM (the concentration of **1**: 10 wt%) under 365 nm light irradiation at room temperature in the solid state, respectively. (c) Normalized emission spectra of **1** (red line), absorption spectra of **2a** before 365 nm light irradiation (blue line) and after 365 nm light irradiation (black line) in the solid state, respectively.

To clearly explain photoswitching mechanism of FPM, the absorption and fluorescence spectrum of FPM (the concentration of **1**: 10 wt%) have been examined in the solid state. The absorption and emission spectra of FPM were recorded upon 365 nm light irradiation at room temperature. Fig. 3a, b show that FPM exhibits weak absorption band around 350-470 nm and strong fluorescence emission at 417 nm before 365 nm light irradiation, which correspond to the absorption spectrum of **2a** and fluorescence emission peak of **1**, respectively. Once 365 nm light irradiation, FPM can be observed that an absorbing band of **2b** is increasing around 350-470 nm, which is assigned to the

formation of keto-form isomer of **2a** in Fig. 3a. When prolonging irradiation time, the emission peak of 417 nm is gradually diminishing in Fig. 3b. Once the absorption spectra of FPM increases to the maximum value, which suggests that the energy transfer rate is basically maximized between **1** and **2b** in FPM. The phenomenon convincingly testifies that the quenching of fluorescence will occur via energy transfer between pyrazolones dye and the keto-form isomer of photochromic pyrazolones as expected. When the fluorescent emission band of pyrazolones dye overlaps well with the absorption spectrum of the keto-form isomer of photochromic pyrazolones unit (Fig. 3c). Therefore, the fluorescence emission of **1** is modulated efficiently by the photoisomerization of **2a** with 365 nm light irradiation.³⁰ When the FPM was heated, the reverse reaction happened from keto-form isomer to enol-form isomer and the absorption band around 350–470 nm was gradually diminishing, and the absorption band recovered completely to the original absorption band intensity, which owes to the excellent fatigue resistance, thermally reversible properties, and rapid response time of **2a** in pure solid state. In agreement with the experiments of naked eye observation, these results evidently demonstrate that photochromic pyrazolones works as a modulator for fluorescence modulation of the pyrazolones dye.

3.4 Fatigue resistance of FPM

The fatigue resistance of FPM was detailedly studied as follows: Firstly, the repeatability of the photoreaction of FPM was assessed. The absorption spectra of FPM (the concentration of **1**: 37 wt%, 10 wt% and 4 wt%) were also measured upon 365 nm light irradiation and heating, respectively (Fig. 4a). When the concentration of **1** is 4 wt% and 10 wt%, the absorption spectra of FPM is reversible and could go through more than 10 cycles. The result indicates the photochromic reaction of **2a** is not obviously affected by the presence of **1** in FPM. Secondly, if the fluorescence photoswitching of FPM is also reversible, when varies the amount of pyrazolones dye in photochromic pyrazolones system. FPM with different doping ratios of **1** was synthesized and their fluorescence photoswitching property were measured too (Fig. S5). The fluorescence intensity of FPM returns completely to the initial value after heating at 120 °C, when the concentration of **1** is 4 wt% and 10 wt% (Fig. 4b). It can be seen noteworthy that the fluorescence photoswitching of

FPM is reversible. So the fluorescence photoswitching efficiency of FPM is remarkably improved by controlling reasonable doping

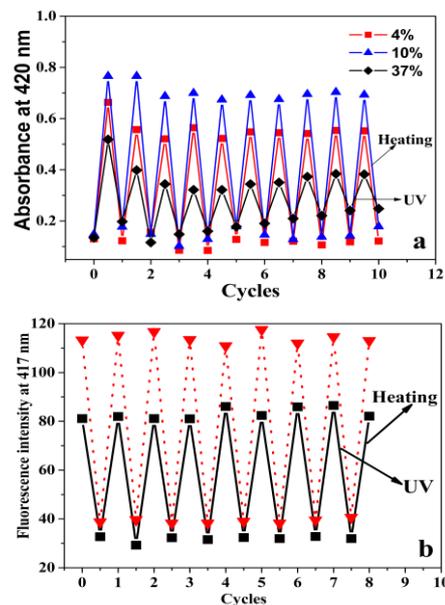


Fig. 4 (a) Absorption spectra cycles of FPM (the concentration of **1**: 37 wt%, 10 wt% and 4 wt%) during alternating 365 nm light irradiation and colour fading at 120 °C in the solid state. (b) Fluorescence photoswitching cycles of FPM ($\lambda_{\text{ex}} = 330$ nm) (the concentration of **1**: 4 wt% (solid line) and 10 wt% (dash line)) during alternating irradiation of 365 nm light and colour fading at 120 °C in the solid state.

ratio, which also confirms that the **2a** regulates the fluorescence of **1** “on” and “off”. The degradation of fluorescence photoswitching function of FPM was not observed obviously after several months storage. The results indicate that fluorescence emission of **1** is efficiently modulated by the photochemical reaction of **2a** with high fluorescence quenching efficiency and remarkable fatigue resistance in the solid state. The highly optical sensitivity, excellent fatigue resistance and high contrast fluorescence photoswitching properties of FPM are foundation for designing novel optoelectronic devices.³¹⁻³⁴

4. Conclusions

In conclusion, we have developed a convenient method for fluorescence switching of pyrazolones dye, whose fluorescence modulation is realized by energy transfer between fluorescence dye and keto-form isomer of photochromic pyrazolones under alternate 365 nm light irradiation and heating at 120 °C. The fluorescence photoswitching materials can work reversibly without obviously degradation. The advantages of our system are based on: 1) The pyrazolones dye synthesized shows fluorescence property and optical waveguide performance, and the

fluorescence of pyrazolones dye is successfully modulated by the photoisomerization of photochromic pyrazolones in the solid state. 2) The fluorescence photoswitching of fluorescence photoswitching materials have been demonstrated to be reversible, and the fluorescence photoswitching cycles could be repeated many times. 3) This study indicates that fluorescence photoswitching materials retain the photochromic properties of pyrazolones and fluorescence, optical waveguide property of pyrazolones dye completely. Hence, fluorescence photoswitching materials are expected to exploit the applications value of pyrazolones dye and photochromic pyrazolones system.

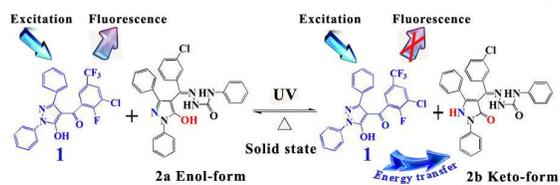
Acknowledgements

This work was supported by Scientific Research Program of the Higher Education Institution of Xinjiang (XJEDU2012I04), the National Natural Science Foundation of China (21262038 and U1203292), Specialized Research Fund for the Doctoral Program of Higher Education (2011650113001), the Outstanding Youth Natural Science Foundation of Xinjiang Uygur Autonomous Region of China (201311006), Doctoral Fund of Xinjiang University (BS110110).

Notes and references

Key laboratory of material and technology for clean energy, ministry of education; Key laboratory of advanced functional materials, autonomous region; Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang, P. R. China. Tel.: +86-991-8583083; Fax: +86-991-8588883; E-mail address: jd:0991@gmail.com

- S. Z. Pu, D. H. Jiang, W. J. Liu, G. Liu and S. Q. Cui, *J. Mater. Chem.*, 2012, **22**, 3517-3526; F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327-336; I. Yildiz, E. Deniz, F. M. Raymo, *Chem. Soc. Rev.*, 2009, **38**, 1859-1867.
- K. Suzuki, T. Ubukata and Y. Yokoyama, *Chem. Commun.*, 2012, **48**, 765-767.
- X. J. Luo and C. Yang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7892-7902.
- W. Wan, M. Q. Zhu, Z. Tian and A. D. Li, *J. Am. Chem. Soc.*, 2015, **137**, 4312-4315.
- Y. Chen and N. Xie, *J. Mater. Chem.*, 2005, **15**, 3229-3232.
- D. Iacopino and G. Redmond, *Chem. Commun.*, 2011, **47**, 9170-9172.
- A. Spangenberg, R. Metivier, R. Yasukuni, K. Shibata, A. Brosseau, G. Johan, A. Jean, P. Yu, T. Asahi and K. Nakatani, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9670-9678.
- K. Xu, J. Zhao, X. Cui and J. Ma, *Chem. Commun.*, 2015, **51**, 1803-1806.
- G. Y. Jiang, S. Wang, W. F. Yuan, Z. Zhao, A. J. Duan, C. M. Xu, L. Jiang, Y. L. Song and D. B. Zhu, *Eur. J. Org. Chem.*, 2007, **13**, 2064-2067.
- S. Kawata and Y. S. Kawata, *Chem. Rev.*, 2000, **100**, 1777-1788.
- Z. Lu, Y. Liu, W. Hu, X. W. Lou and C. M. Li, *Chem. Commun.*, 2011, **47**, 9609-9611.
- T. Kowada, J. Kikuta, A. Kubo, M. Ishii, H. Maeda, S. Mizukami and K. Kikuchi, *J. Am. Chem. Soc.*, 2011, **133**, 17772-17776.
- Y. Osakada, L. Hanson and B. Cui, *Chem. Commun.*, 2012, **48**, 3285-3287.
- S. C. Pang, H. Hyun, S. Lee, D. Jang, M. J. Lee, S. H. Kang and K. H. Ahn, *Chem. Commun.*, 2012, **48**, 3745-3747; A. A. Beharry, G. A. Woolley, *Chem. Soc. Rev.*, 2011, **40**, 4422-4437.
- R. N. Dsouza, U. Pischel and W. M. Nau, *Chem. Rev.*, 2011, **111**, 7941-7980.
- Z. Huang, J. Ren and X. Qu, *Mol. Biosyst.*, 2012, **8**, 921-926.
- J. Bruce, *Annual. Reports. Section "B" (Organic Chemistry)*, 2007, **103**, 370-391; S. van de Linde, M. Sauer, *Chem. Soc. Rev.*, 2014, **43**, 1076-1087.
- J. X. Guo, L. Liu, G. F. Liu, D. Z. Jia and X. L. Xie, *Org. Lett.*, 2007, **9**, 3989-3992.
- L. Song, Y. Yang, Q. Zhang, H. Tian and W. Zhu, *J. Phys. Chem. B*, 2011, **115**, 14648-14658.
- C. J. Yun, J. You, J. Kim, J. Huh and E. Kim, *J. Physiol. Biochem. C: Rev. Chem.*, 2009, **10**, 111-129.
- M. Irie, T. Fukaminato, T. Sasaki, Naoto Tamai and K. Tsuyoshi, *Nature*, 2002, **420**, 759-760.
- B. Liao, W. Wang, P. Long, X. T. Deng, B. Q. He, Q. Q. Liu, S. J. Yi, *Carbon*, 2015, **91**, 30-37.
- S. A. Diaz, F. Gillanders, E. A. Jares-Erijman, T. M. Jovin, *Nature communications*, 2015, **6**, 1-11.
- L. Liu, X. Y. Xie, D. Z. Jia, J. X. Guo and X. L. Xie, *J. Org. Chem.*, 2010, **75**, 4742-4747.
- H. Liu, J. X. Guo, D. Z. Jia, M. X. Guo, F. L. He, L. Liu, D. L. Wu and F. Li, *J. Solid State Chem.*, 2014, **216**, 73-78.
- R. L. Zhang, Y. S. Wu, Z. L. Wang, W. Xue and H. B. Fu, *J. Phys. Chem. C*, 2009, **113**, 2594-2602.
- C. Zhang, Y. S. Zhao and J. N. Yao, *New J. Chem.*, 2011, **35**, 973-978.
- B. S. Jensen, *Acta. Chem. Scand.*, 1959, **13**, 1668-1670.
- D. Heinert and A. E. Martell, *J. Am. Chem. Soc.*, 1962, **84**, 3257-3262.
- I. Yildiz, E. Deniz and F. M. Raymo, *Chem. Soc. Rev.*, 2009, **38**, 1859-1867.
- H. Dong, H. Zhu, Q. Meng, X. Gong and W. Hu, *Chem. Soc. Rev.*, 2012, **41**, 1754-1708.
- P. Heremans, G. H. Gelinck, R. Muller, K. J. Baeg, D. Y. Kim and Y. Y. Noh, *Chem. Mater.*, 2011, **23**, 341-358.
- Z. F. Liu, K. Hashimoto and A. Fujishima, *Nature*, 1990, **347**, 658-660.
- H. Mustroph, M. Stollenwerk and V. Bressau, *Angew. Chem. Int. Ed.*, 2006, **45**, 2016-2035.



Photochromic pyrazolones is exploited as a modulator to toggle fluorescence of dye “on” and “off” based on energy transfer.