Journal of
Materials Chemistry

Cite this: *J. Mater. Chem.*, 2011, **21**, 3210

www.rsc.org/materials

PAPER

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

Jixi Guo,[a] Dianzeng Jia,*[a] Lang Liu,[a] Hui Yuan[a] and Feng Li[b]

Received 25th September 2010, Accepted 10th December 2010
DOI: 10.1039/c0jm03216f

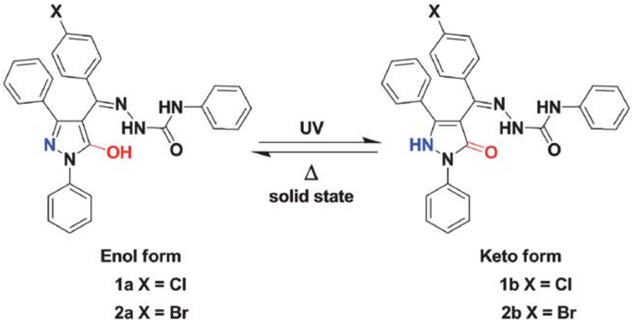
Photochromic compounds derived from pyrazolones, which undergo reversible photoisomerization reactions in pure solid state, were synthesized toward the end of designing novel solid-state photonic switches. The materials exhibit high sensitivity, excellent fatigue resistance and reversible fluorescent switching properties with distinguishable contrast signals under alternating UV irradiation and heating. The mechanism of the photochromic reactions was verified by FT-IR and XPS. The detailed analysis of the spectra and crystal structure of the materials revealed that their photochromism resulted from tautomerization between their enol and keto forms accompanied by proton transfer.

Introduction

Photochromism has attracted considerable attention since its discovery in 1867[1] and has been investigated extensively for diverse applications such as optical data storage and switches related to photochromism.[2,3] Toward the end of tuning optical properties of materials, a variety of organic photochromic compounds have been developed successfully through molecule design.[4] However, most of the materials only exhibit a photochromic effect in solution.[5] It is rather rare to find single component solid-state photochromism in reports so far, whereas constructing optical switches based on materials in solid state is indispensable for practical applications of optical switches. Recently, photochromic materials were thus dispersed into polymer matrices or sol–gel media for realizing complex solid-state photochromism and overcoming the difficulty related to the photochromic effect in solution.[6] The strategies, however, are still limited by suppressed photochromic reactivity and quantity of active materials dispersed in polymer matrices.[7] It is highly desirable to develop new photochromic systems in solid state and even in single crystalline state for designing highly efficient photonic memories and photonic switches.[8]

In our previous paper, we have designed and synthesized a series of photochromic compounds derived from pyrazolone condensed with thiosemicarbazide derivatives.[9] Upon irradiation with UV light of 365 nm, the materials can change their color from white to yellow, and then partly return to white again by keeping in visible light or heating. Unfortunately, their performances still cannot meet the requests in optical devices concerned with reversibility and stability for practical application. It is still a challenge to develop new photochromic compounds with high sensitivity and excellent fatigue resistance.

Herein, we successfully designed two new photochromic compounds of **1a** and **2a** (Scheme 1), which exhibit highly improved reversible photoisomerization reactions under alternating UV light irradiation and heating in solid state, produced by condensing phenylsemicarbazide with pyrazolones. The materials exhibit much higher optical sensitivity and fatigue resistance in solid state, compared to those synthesized in our lab previously.[9,10] The fluorescent emissions of the new compounds undergo reversible "on" and "off" with high contrast signals after irradiation with UV light of 365 nm and heating at 120 °C, respectively. The materials are thus promising building blocks to



Scheme 1 Photochromic reactions of **1** and **2**

---

[a] *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. E-mail: jdz0991@gmail.com; Fax: +86-991-8588883; Tel: +86-991-8583083*
[b] *CBEN and Department of Chemistry, Rice University, Houston, TX, 77081, USA*

† Electronic supplementary information (ESI) available: Photographs of photochromic single crystal of **1a**, normalized emission spectra and XRD spectra of powders for **1** and **2**, Selected bond length, bond angles data, hydrogen bonds and crystallographic information files (CIF) for **1a**. CCDC reference number 680802. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0jm03216f

construct optical storage devices and switches. In order to further understand and verify the mechanism of the photochromic reactions of **1a** and **2a**, FT-IR and XPS were used to investigate their structure changes before and after UV irradiation. In addition, the crystallographic analysis of colorless crystal of **1a** has also been carried out for studying the photochromic process. The results indicate that the photochromism arises from proton transfer from the O atom of hydroxyl group to the N atom of pyrazole-ring, accompanying their structure change from enol form (*E*-form) to keto form (*K*-form) as shown in Scheme 1. The fascinating systems could eventually lead to realizing novel devices for photonic applications.

Experimental

General

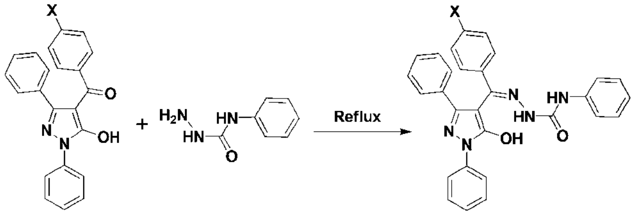
^{1}H NMR spectra were performed on an INOVA-400 NMR spectrometer with DMSO-d_6 as solvent. Mass spectrum was determined with HP1100 LC-MS using electrospray ionization mass spectrometry. Melting point was measured with a TECH XT-5 melting point apparatus. The elemental analyses were made on FLASH EA 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 a Hitachi F-4500 fluorescence spectrophotometer. FT-IR spectra were recorded by using infrared diffuse reflectance spectroscopy 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 (1.5 W cm^{-2}) and a TECH XT-5 melting point apparatus were used as sources for photocoloration and thermbleaching, respectively. Powder X-ray diffraction (XRD, MXP18AHF, MAC, Japan) using Cu-Kα radiation ($\lambda = 1.54056$ Å) was used to identify the as-synthesized powders. Photochromic reaction of powders (crystalline state, the size of crystal grain is 26 nm and 34 nm for **1a** and **2a**, respectively) were all characterized at room temperature.

Materials

1.3-Diphenyl-5-pyrazolone (DPP) was synthesized with the method described in the literature.[11] 4-Phenylsemicarbazide (PSC), 4-chlorobenzoylchloride and 4-bromobenzoylchloride were purchased from the Aldrich Company, USA. Other materials were purchased from commercial sources, and the solvents were purified with standard procedures.

1,3-diphenyl-4-(4-chlorobenzal)-5-pyrazolone (DP4ClBP) and 1,3-diphenyl-4-(4-bromobenzal)-5-pyrazolone (DP4BrBP) were synthesized by the method reported.[12] For DP4ClBP. Yield: 73%. Mp. 155.4–156.8 °C. Elemental analysis calcd for $C_{22}H_{15}N_2O_2Cl$: C, 70.50; H, 4.03%; N, 7.47. Found: C, 70.48; H, 4.42%; N, 7.50. For DP4BrBP. Yield: 69%. Mp. 147.4–148.5 °C. Elemental analysis calcd for $C_{22}H_{15}N_2O_2Br$: C, 63.02; H, 3.61; N, 6.68%. Found C, 62.95; H, 3.57; N, 6.71%.

1,3-Diphenyl-4-(4-chlorobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (**1**). DP4ClBP (3 mmol) and PSC (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 (Scheme 2). 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: 84%. Mp. 204.2–205.1 °C. δ_H(400 MHz, DMSO-d_6, 25 °C, TMS): 12.016 (1H, Pz–OH), 9.842 (1H, N5–H), 9.128 (1H, N4–H), 7.945–6.985 (19H, phenyl-ring). ν_{max}/cm^{-1}: 3359 3340 υ(N–H), 1651 υ(C=O), 1600 υ(C=N), 1556, 1507 υ(phenyl), 1520, 1454 υ(pyrazole-ring). MS: *m*/*z* M$^+$: 507.80. Elemental analysis calcd for $C_{29}H_{22}N_5O_2Cl$: C, 68.57; H, 4.37; N, 13.79%. Found C, 68.50; H, 4.42; N, 13.67%.1,3-diphenyl-4-(4-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (**2**). Compound **2** was synthesized with the method similar to the preparation of compound **1**. Yield: 81%. Mp. 201.1–202.3 °C. δ_H(400 MHz, DMSO-d_6, 25 °C, TMS): δ 11.963 (1H, Pz–OH), 9.817 (1H, N5–H), 9.115 (1H, N4–H), 7.935–6.955 (19H, phenyl-ring). ν_{max}/cm^{-1}: 3364 3333 υ(N–H), 1650 υ(C=O), 1600 υ(C=N), 1556, 1508 υ(phenyl), 1522, 1453 υ(pyrazole-ring). MS: *m*/*z* M$^+$: 552.10. Elemental analysis calcd for $C_{29}H_{22}N_5O_2Br$: C, 63.05; H, 4.01; N, 12.68%. Found C, 63.15; H, 3.92; N, 12.66%.



Scheme 2 Synthesis of the pyrazolones **1a** and **2a**

Results and discussion

The two new compounds **1** and **2** undergo reversible photocoloration and thermalbleaching reactions in pure solid state. Upon irradiation with light of 365 nm, the *E*-form of **1a** and **2a** were converted to *K*-form **1b** and **2b**, respectively, accompanied by distinguishable changes in the absorption spectra as shown in Fig. 1. The systems can then be decolored by heating at 120 °C. After white **1a**, for example, changed into yellow **1b** under UV irradiation, a strong and broad absorption band centered at 409 nm appeared in Fig. 1A. The absorption at 409 nm disappeared instantaneously after heating at 120 °C, and the initial color and spectrum of the materials were completely recovered. The photochemical process exhibits perfect reversibility. Compound **2a** also underwent excellent photochromic reaction under UV irradiation of 365 nm light. A new absorption band centered at 399 nm, which corresponds to the *K*-form of **2b**, appeared in the absorption spectra in Fig. 1B, and this process was accompanied by a distinct color change from white to yellow. The absorption band disappeared again after the sample was heated at 120 °C and the original absorption spectrum was fully recovered. After comparing the absorption band of **2b** with that of **1b**, we found that the absorption band was blue shifted by as much as 10 nm. This could result from the reduced π-conjugation system for the substituent on phenyl of the 4-position of pyrazolone-ring changing from Cl to Br. The insert charts in Fig. 1A and 1B show that there is no significant degradation detected by absorption for **1** and **2**, respectively, after alternatively photo-coloring and thermal-bleaching for 15 cycles. The results indicate that the photochromism of pyrazolones **1** and **2**

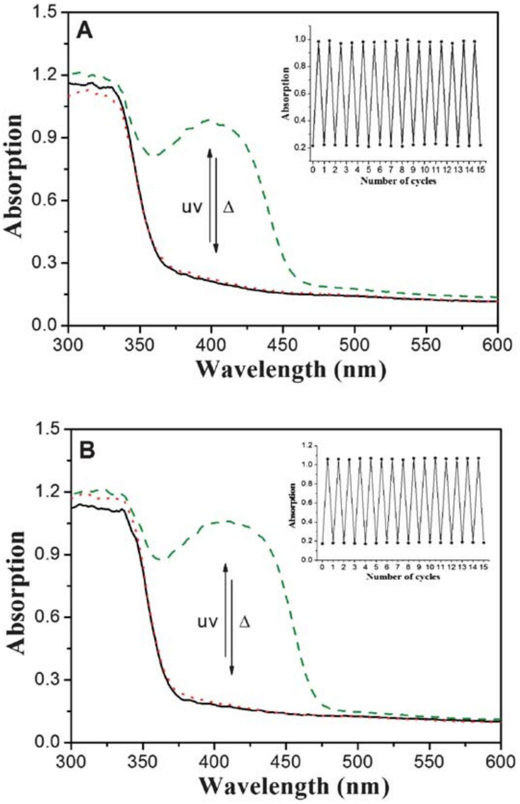


Fig. 1 Absorption spectra of **1** (A) and **2** (B): before irradiation with 365 nm light at room temperature (solid line), after UV irradiation (dashed line), and then after thermal bleaching at 120 °C (dotted line). The inset in (A) and (B) shows photocoloration-thermalbleaching cycles upon alternating irradiation with UV light and heating for **1** and **2**, respectively.

exhibit highly improved fatigue resistance and sensitivity in solid state, which is critical to achieve designing information storage devices and optical switches, compared to photochromic materials reported so far.[9,13] It is interesting to find that both pyrazolones **1** and **2** are photochromic in the solid state, but not in solution.

We further investigated the fluorescent properties (Fig. 2) of the two compounds during their photochromic reaction in solid state. A characteristic fluorescence band was observed at 370 nm by 260 nm excitation for the *E*-form **1a**. Upon irradiation with 365 nm light, the intensity of the fluorescence band decreased dramatically, and it reached the photostationary state of *K*-form **1b** with fluorescence on/off ratio of 6 : 1 after 8 min in accompanying with blue-shift of the band of 7 nm. The fluorescence intensity of the materials returned fully to the initial state after heating at 120 °C. In comparison, compound **2a** also showed similar emission behavior after irradiation with UV light and excited at 260 nm, but with blue shift of 4 nm. It is noteworthy that the fluorescence on/off ratio of **2a** reaches 10 : 1, which highlights the much improved high contrast ratio. The change should be attributed to photoinduced transformation from *E*-form to *K*-form by proton transfer, which resulted in changes of the π conjugation system in the two compounds. These results indicate that fluorescent switches have been realized successfully by irradiation with UV light and heating based on photochromic reaction of **1a** and **2a** in solid state for the first time. The highly improved optical sensitivity and fatigue resistance of the two compounds in solid state together with their highly enhanced contrast fluorescent switching properties are promising for designing novel optical devices.

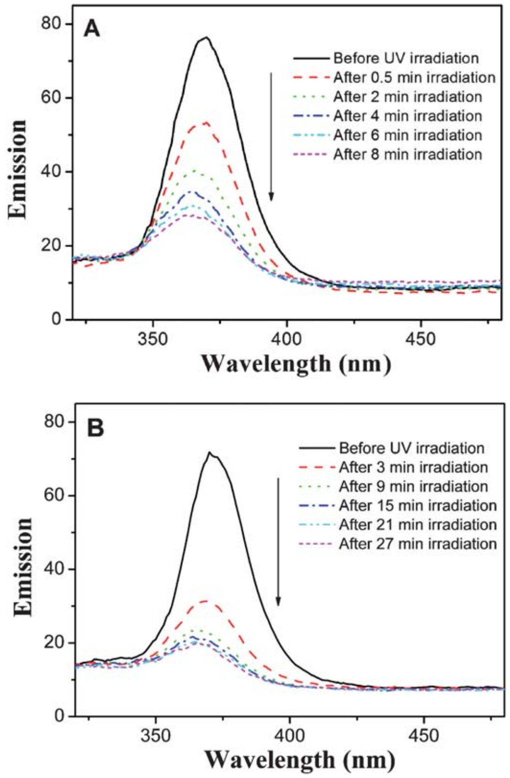


Fig. 2 Fluorescence changes of **1** (A) and **2** (B) with UV irradiation (λ_{ex} = 260 nm).

With the aim of understanding the mechanism of the photochromic reaction of **1a** and **2a**, we investigated the structural origin of their drastic color changes in solid state with IR spectra (Fig. 3). The structure differences between their *E*-form and *K*-form resulted in spectra changes in the range of 3000–3500 cm^{-1} clearly. Under irradiation of 365 nm light, a new sharp band attributed to the N–H stretching vibration appears at 3387 cm^{-1} for the formation of *K*-form **1b** along with relative intensity decrease of a smooth band at 3252 cm^{-1} (Fig. 3A). The band of 3252 cm^{-1} can be ascribed to O–H vibration due to the red shift induced by the strong hydrogen bonds in solid state. There are no significant changes in the region of 650–2000 cm^{-1}. Due to the functional group C═O in the side tail of **1** and **2** also shows a strong stretching vibration at 1651 cm^{-1}, which obscure the vibration change in the characteristic region attributed to the structure change from C–O to C═O, it is unavailable for us to monitor the change of the C–O bond. Compound **2** shows similar spectra changes under UV light of 365 nm. A new sharp band attributed to N–H stretching vibration appears at 3386 cm^{-1} in accompanying with decreased relative intensity of a smooth band at 3259 cm^{-1}. The results strongly support our suggested photochromism mechanism here and in our previous reports.[9c] Pyrazolones convert from the *E*-form to *K*-form accompanied by proton transfer after irradiation with UV light of 365 nm.

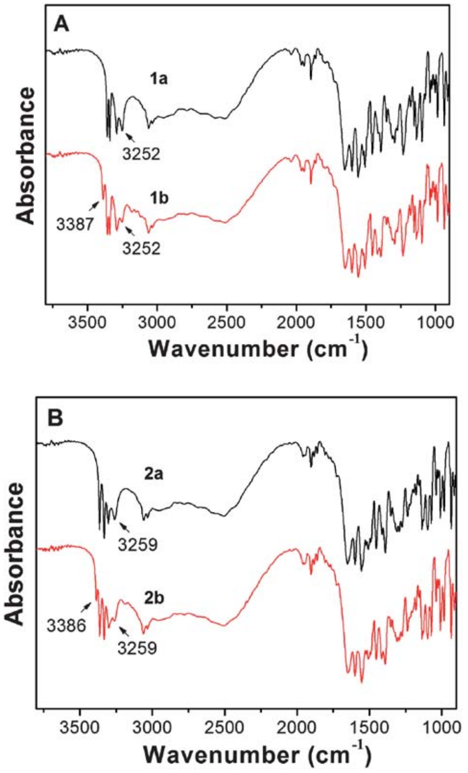


Fig. 3 (A) FT-IR spectra of **1**, before UV irradiation (black), after UV irradiation (grey). (B) FT-IR spectra of **2**, before UV irradiation (black), after UV irradiation (grey).

While IR spectra is a useful method to study the hydrogen bonded structure, it cannot give definite structure change corresponding to the O–H stretching band. However, binding energies of the spectral features are sensitive to the chemical environment perturbation, and it is possible to distinguish the tautormers in pyrazolones. Hence, XPS was considered as a powerful tool to study the tautomerism problem in hydrogen bonded system.[14] In our experiment we focus our efforts on examining the O 1s spectra changes for further verifying the photochromic mechanism proposed. The O 1s XPS spectra of **1** and **2** are shown in Fig. 4, which can be decomposed into two peaks by curve fitting. The first O 1s peak which occurs at 532.7 eV and 532.8 eV for our samples are assigned to oxygen atoms of C–O group, and the second peak corresponding to binding energy values 530.6 eV and 530.7 eV are ascribed to oxygen atoms of C=O group for **1** and **2**, respectively. The relative amounts of the tautomers can be estimated from *E*-form/*K*-form isomers ratio of 55 : 45 for **1a**, and 45 : 55 for **2a** before irradiation. It is clearly observed that the *E*-form/*K*-form isomers ratio changed to 34 : 66 for **1b** and **2b** after UV irradiation. The populations of C=O increased along with decreasing of C–O after illuminated by UV light of 365 nm, which directly indicates that the white *E*-form **1a** and **2a** transform to *K*-form **1b** and **2b** during the photochromic process. The XPS results are consistent with those from FT-IR spectra, and thus further confirm the suggested mechanism of photochromic pyrazolones. Based on IR and XPS spectra results, we can safely conclude that the photochromism of pyrazolones is due to tautomerization between *E*-form and *K*-form by phototriggered proton transfer.

Compound **1** not only shows photochromism in powders, but also in macroscopic single crystal. In order to further verify the mechanism of photochromic pyrazolones, we tried to obtain crystal structure information changing in accompanying with the photochromism in single crystal using single crystal X-ray diffraction, but failed for the low population of the *K*-form species in the single crystal under ordinary UV irradiation. Only the structure of the *E*-form of pyrazolone **1a** before irradiation was determined (Fig. 5). Single crystal of **1a** suitable for X-ray diffraction analysis was obtained by slow evaporation of their ethanol solution at room temperature in the dark. The crystal of **1a** belongs to a monoclinic system, $P2_1/c$.[15] There are two non-centrosymmetric molecules of **1a** in the asymmetric unit, but conformations of the two molecules differ slightly. The length of C–O bond of pyrazolone-ring is 1.336 and 1.328 Å in the two molecules, respectively, which is consistent with the length of C–O single bond. However, the length of C–O bond of phenylsemicarbazone is 1.252 and 1.244 Å, respectively, which is in accordance with the length of C=O double bond. It can be deduced that the structure of **1a** is the *E*-form in the colorless

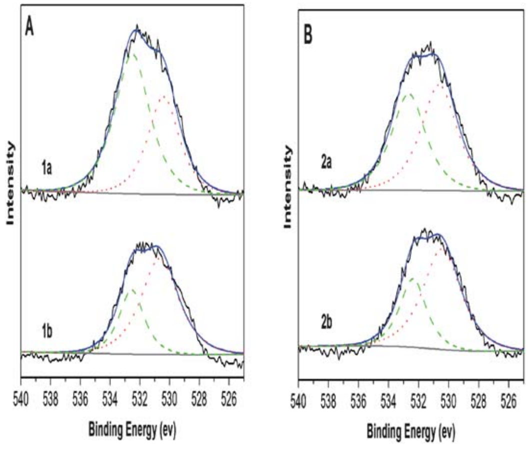


Fig. 4 (A) O 1s spectra (XPS) of **1**, before irradiation with UV light (top), after irradiation (bottom). (B) O 1s spectra (XPS) of **2**, before irradiation with UV light (top), after irradiation (bottom).

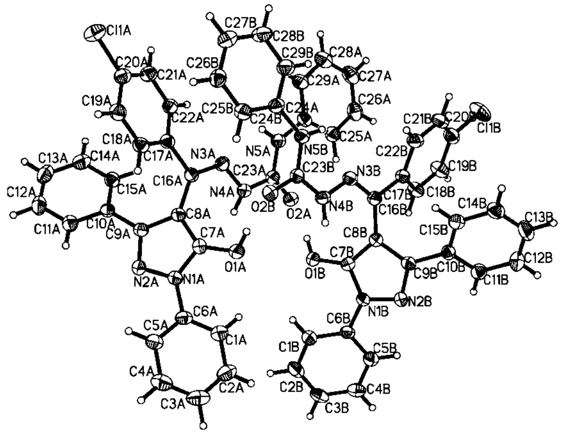


Fig. 5 Molecular structure of **1a** with the atom numbering. The ellipsoid represents 50% displacement of atoms.

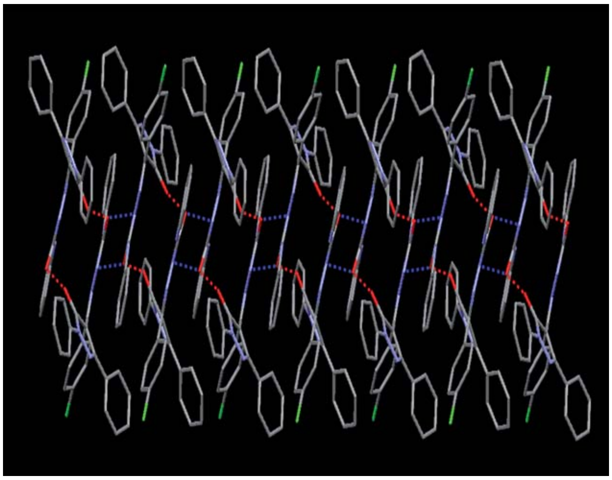


Fig. 6 One-dimensional hydrogen-bonded chains in the crystal structure of **1a**, all the H atoms are omitted for clarity.

crystal before UV irradiation, which is similar to the other pyrazolones with phenylsemicarbazone compounds.[9b] As shown in Fig. 6, 1D chains are formed by linking the adjoining molecules through typical intermolecular hydrogen bonds. Firstly, dimers consisting of two non-centrosymmetric molecules are built by intermolecular hydrogen bonds (O1A–H···O2B, 2.560(2) Å, 173(4)° and O1B–H···O2A, 2.589(2) Å, 170(4)°), and then 1D chains are formed by connecting those dimmers by other intermolecular hydrogen bonds (N4A–H···O2A′, 3.114(3) Å, 151(2)° and N4B–H···O2B′, 3.050(3) Å, 135(2)°). There are no direct hydrogen bonds between the O atom and N atom of the pyrazolone-ring through analysis of the hydrogen bonding in the structure. Based on the single crystal structure information, we further suggest that intermolecular double proton transfer through formed 1D chains with structure rearrangement may be attributed to the enol-keto tautomerization process of photochromic pyrazolones. The theoretical studies and further investigation on determining the photocolored structures by X-ray crystallographic analysis using advanced two photon excitation technique are now in progress in our group.

Conclusions

Two novel pyrazolones (**1** and **2**), which exhibit greatly improved photochromic properties, have been synthesized successfully by introducing a phenylsemicarbazide unit. They show excellent fatigue resistance and distinguished contrast fluorescence emission signals in the solid state. The mechanism of the photochromic reactions was due to tautomerization between their enol and keto forms accompanied by proton transfer, and this process was confirmed by FT-IR and XPS. The progress provides a new insight for the design and synthesis of perfect photochromic compounds in solid state and even in macroscopic single crystal. The excellent photochromic performance of the new pyrazolones can satisfy the fundamental requirements for designing new optoelectronic devices, such as optical memories and switches.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21062020 20866009 and 20762010), the Natural Science Foundation of Xinjiang Uygur Autonomous Region of China (2009211B02) and Scientific Research Program of the Higher Education Institution of Xinjiang (XJEDU2008S08) and SRFDP20070755001.

Notes and references

1 M. Fritsche, *Comp. Rend.*, 1867, **69**, 1035.

2 H. Dürr and H. Bouas-Laurent, *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, The Netherlands, 1990; S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777; C. C. Corredor, Z. L. Huang and K. D. Belfield, *Adv. Mater.*, 2006, **18**, 2910; G. Y. Jiang, S. Wang, W. F. Yuan, L. Jiang, Y. L. Song, H. Tian and D. B. Zhu, *Chem. Mater.*, 2006, **18**(2), 235.

3 Y. Yokoyama, *Chem. Rev.*, 2000, **100**, 1717; G. Berkovic, *Chem. Rev.*, 2000, **100**, 1741; Y. C. Jeong, D. G. Park, I. S. Lee, S. I. Yang and K. H. Ahn, *J. Mater. Chem.*, 2009, **19**, 97; C. Weber, F. Rustemeyer and H. Dürr, *Adv. Mater.*, 1998, **10**, 1348; J. Areephong, T. Kudernac, J. J. D. D. Jong, G. T. Carroll, D. Pantorott, J. Hjelm, W. R. Browne and B. L. Feringa, *J. Am. Chem. Soc.*, 2008, **130**, 12850; N. Xie and Y. Chen, *J. Mater. Chem.*, 2007, **17**, 861; L. Y. Zhu, W. W. Wu, M. Q. Zhu, J. J. Han and J. K. Hurst, *J. Am. Chem. Soc.*, 2007, **129**, 3524.

4 K. Matsuda and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 8309; T. B. Norsten and N. R. Branda, *J. Am. Chem. Soc.*, 2001, **123**, 1784; K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura and M. Irie, *Angew. Chem.*, 2006, **118**, 6620; P. Naumov, K. Sakurai, Y. Ohashi and S. W. Ng, *Chem. Mater.*, 2005, **17**, 5394; B. Wüstenberg and N. R. Branda, *Adv. Mater.*, 2005, **17**, 2134; W. Zhao and E. M. Carreira, *Org. Lett.*, 2006, **8**(1), 99; R. F. Khairutdinov, K. Giertz, J. K. Hurst, E. N. Voloshina, N. A. Voloshin and V. I. Minkin, *J. Am. Chem. Soc.*, 1998, **120**, 12707; J. Areephong, H. Logtenberg, W. R. Browne and B. L. Feringa, *Org. Lett.*, 2010, **12**(9), 2132.

5 Y. Kishimoto and Jiro Abe, *J. Am. Chem. Soc.*, 2009, **131**, 4227; Y. Chen and D. X. Zeng, *J. Org. Chem.*, 2004, **69**, 5037; R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Nather, F. Renth and F. Temps, *J. Am. Chem. Soc.*, 2009, **131**, 15594.

6 K. Uchida, M. Saito, A. Murakami, S. Nakamura and M. Irie, *Adv. Mater.*, 2003, **15**, 121; T. Tsujioka, M. Kume and M. Irie, *J. Photochem. Photobiol., A*, 1997, **104**, 203; R. Pardo, M. Zayat and D. Levy, *J. Mater. Chem.*, 2009, **19**, 6756; R. Métivier, S. Badré, R. Méallet-Renault, P. Yu, R. B. Pansu and K. Nakatani, *J. Phys. Chem. C*, 2009, **113**, 11916; S. Z. Xiao, Y. Zou, M. X. Yu, T. Yi, Y. F. Zhou, F. Y. Li and C. H. Huang, *Chem. Commun.*, 2007, 4758; D. Levy, *Chem. Mater.*, 1997, **9**, 2666; J. Whelan, J. T. C. Wojtyk and E. Buncel, *Chem. Mater.*, 2008, **20**, 3797.

7 M. Irie, *Chem. Rev.*, 2000, **100**, 1685; H. Tian and S. Wang, *Chem. Commun.*, 2007, 781.

8 E. Hadjoudis and I. Mavridis, *Chem. Soc. Rev.*, 2004, **33**, 579; K. Amimoto and T. Kawato, *J. Photochem. Photobiol., C*, 2005, **6**, 207; T. Yamada, S. Kobatake, K. Muto and M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 1589; J. Harada, R. Nakajima and K. Ogawa, *J. Am. Chem. Soc.*, 2008, **130**, 7085; I. Yildiz, E. Deniz and F. M. Raymo, *Chem. Soc. Rev.*, 2009, **38**, 1859.

9 J. X. Guo, L. Liu, G. F. Liu, D. Z. Jia and X. L. Xie, *Org. Lett.*, 2007, **9**, 3989; X. Y. Xie, L. Liu, D. Z. Jia, J. X. Guo, D. L. Wu and X. L. Xie, *New J. Chem.*, 2009, **33**, 2232; J. X. Guo, L. Liu, D. Z. Jia, J. H. Wang and X. L. Xie, *J. Phys. Chem. A*, 2009, **113**(7), 1255; B. H. Peng, G. F. Liu, L. Liu and D. Z. Jia, *Tetrahedron*, 2005, **61**, 5926; T. Zhang, G. F. Liu, L. Liu, D. Z. Jia and L. Zhang, *Chem. Phys. Lett.*, 2006, **427**, 443.

10 L. Liu, X. Y. Xie, D. Z. Jia, J. X. Guo and X. L. Xie, *J. Org. Chem.*, 2010, **75**, 4742.

11 J. Y. Li, X. Y. Wang and Q. H. Zhao, *Chin. J. Chem. Reagen.*, 1997, **19**, 112.

12 B. S. Jensen, *Acta Chem. Scand.*, 1959, **13**, 1668.

13 J. Harada, Y. Kawazoe and K. Ogawa, *Chem. Commun.*, 2010, **46**, 2593; G. Xu, G. C. Guo, M. S. Wang, Z. J. Zhang, W. T. Chen and J. S. Huang, *Angew. Chem., Int. Ed.*, 2007, **46**, 3249; B. Qin, H. Y. Chen, H. Liang, L. Fu, X. F. Liu, X. H. Qiu, S. Q. Liu, R. Song and Z. Y. Tang, *J. Am. Chem. Soc.*, 2010, **132**, 2886;

J. W. Chung, Y. You, H. S. Huh, B. K. An, S. J. Yoon, S. H. Kim, S. W. Lee and S. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 8163.

14 E. Ito, H. Oji, T. Araki, K. Oichi, H. Ishii, Y. Ouchi, T. Ohta, N. Kosugi, Y. Maruyama, Y. Naito, T. Inable and K. Seki, *J. Am. Chem. Soc.*, 1997, **119**, 6336.

15 Crystal data for **1a**: colorless, $C_{29}H_{22}N_5O_2Cl$, M = 507.97 monoclinic, $P2_1/c$, a = 10.982(2), b = 18.017(3), c = 26.297(6) Å, β = 106.586(1)°, V = 4986.39(17) Å3, Z = 8, D_c = 1.353 g cm–3, μ = 0.191 mm–1, F(000) = 2112 and T = 153(2) K. The crystallographic data were collected on an imaging plate system (Rigaku R-AXIS SPIDER) with a graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å, ω-scans, 3.07 ≤ θ ≤ 27.48°). Crystal structures was solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXTL-97* program,9279 unique measured reflections were used in the refinement. All non-H atoms were refined anisotropically. The H atoms on oxygen and nitrogen atoms were located from the Fourier maps, and all of the other H atoms were placed in geometrically idealized positions. The refinement converged to R_1 (observed reflections with $I > 2\sigma(I)$) = 0.0486, wR_2 = 0.1215 and S = 1.112. CCDC deposition number: 680802†.