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COMMUNICATION

Visible Mechanochromic Responses of Spiroprans in Crystal *via* Pressure-Induced Isomerization

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

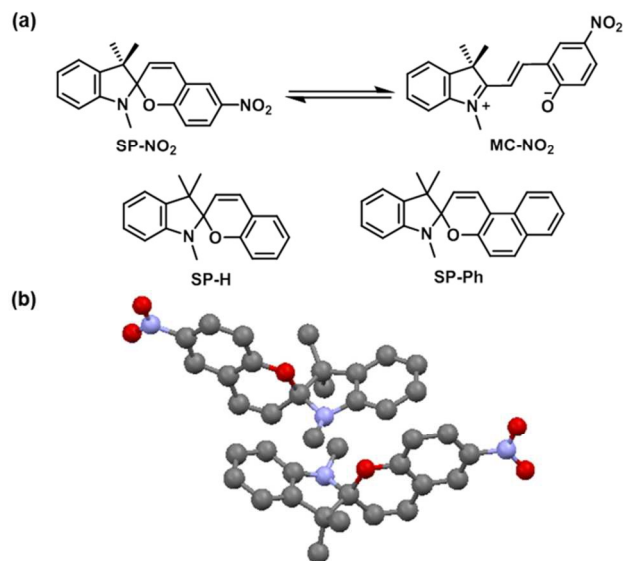
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The isomerization of spiropyrans in crystals was realized under high pressure, and corresponding mechanochromic response was visible to be observed by naked eyes. *In situ* UV-Vis spectroscopy study demonstrated that the equilibrium constant increases with the increasing pressure, from which we proposed that the negative volume of reaction determined the isomerization under high pressure.

Mechanochromic molecules, which are sensitive to mechanical forces, have attracted much attention because of their great potential applications in the field of optoelectronics, such as sensors and memory devices¹⁻⁴. Pressure, as one of the most common natural external stimuli, can cause structural and chemical transformations of the compounds to realize mechanochromic responses⁵⁻⁸. Most researches on mechanochromic responses under pressure focus on the changes of aggregation state⁶ and non-covalent interaction^{5,7,8}. Whereas the mechanochromic responses based on the formation and/or breakage of covalent bonds *via* organic reaction have the potential to achieve pressure-sensing, fabricate *in situ* optical-recording system and memory devices. So far, few examples of high pressure mechanochromic responses based on organic chemical reaction were reported yet. For example, Li *et al.* recently reported the first quantitatively tuned switch by pressure of benzoxazines in crystalline state.⁹ Indeed, high pressure has been successfully employed in facilitating organic reactions¹⁰, such as polymerization of butadiyne¹¹, acetylene^{12,13}, and cyanoacetylene¹⁴, 1,3-dipolar cycloaddition of azide and alkyne^{15,16}, and other systems¹⁷⁻²³. Hence, pressure-induced mechanochromic responses based on organic reaction become a field in need to be studied.

Spiropyrans (SP) are one of the most extensively studied family of compounds in terms of thermochromic²⁴, solvatochromic²⁵, and especially photochromic^{26,27} properties. With UV irradiation, SP in solution or other matrices would transform from a colourless or weakly coloured closed form to a highly coloured open planar merocyanine (MC) form²⁸. This isomerization could be observed by naked eyes and the process was usually monitored by UV-Vis

spectroscopy, in which a new peak emerged in visible region²⁹. Thus, SP could be used in functional materials as optoelectronic properties improvement³⁰, colorimetric temperature indicators²⁴, and chemosensors^{31,32}. However, the chromic responses of SP in solutions were normally complicated by solvents. That impedes their further application and promotes the interest in studying the chromic responses in crystals. So far, unless at very low temperature or after structural modification, the chromic responses in crystals were limited and hardly detected^{27,28}.



Scheme 1. (a) Isomerization and structures of spiropyrans. (b) ORTEP drawings of the crystal structures of SP-NO₂.

The high pressure research has changed dramatically with the development of diamond anvil cells (DACs), which can provide very high pressure³³. More importantly, since diamonds are transparent to radiation extending from the IR into UV, X-ray, and especially the visible region, samples in DACs can be directly observed and

studied spectroscopically *in situ* under high pressure conditions¹⁰. In this report, owing to diamond anvil cells technique, the first example of visible mechanochromism of **SP** in crystals based on their pressure-induced isomerization to **MC** forms was achieved. *In situ* UV-Vis spectroscopy measurement showed equilibrium constant (*K*) increased with the increasing pressure, which was proposed to originate from the negative volume of reaction during the isomerization of **SP** derivatives.

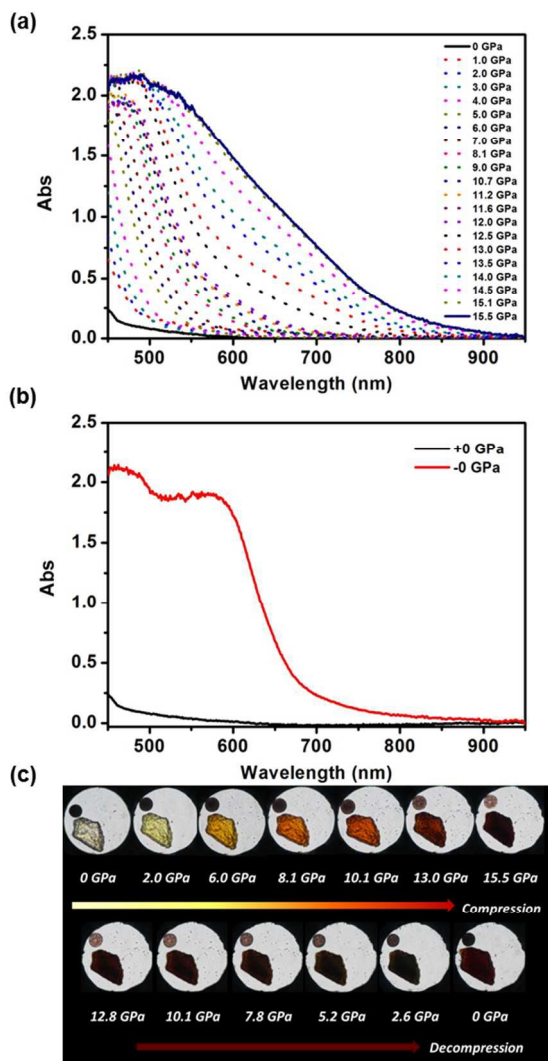


Fig. 1 (a) *In situ* UV-Vis spectroscopy of **SP-NO₂** under compression in the range of 0-15.5 GPa. (b) The comparison of UV-Vis spectroscopy of **SP-NO₂** crystals before (+0 GPa) and after (-0 GPa) the pressure treatment. (c) *In situ* micrographs of **SP-NO₂** crystal under 0-15.5 GPa and 0 GPa after the discharge of pressure.

SP-NO₂ is one of the most commonly studied molecules in **SP** family. It can isomerize to **MC-NO₂** in PMMA matrix³⁴ or in other solutions³⁵ after UV irradiation at *ca.* 365 nm (Scheme 1a). In order to investigate the influence of pressure on the isomerization of **SP** in crystals, **SP-NO₂** was taken as an example to perform the high pressure experiment using symmetric DAC technique at room temperature. The crystals of **SP-NO₂** were obtained, and its X-ray crystal structure was found to be the same with that in the

Cambridge Crystallographic Data Centre (CCDC) (Scheme 1b). Then the *in situ* UV-Vis absorption spectroscopy was performed under different pressures, indicating the chemical changes of the substrate structure (Fig. 1a). It was found that the spectra changed slightly when the pressure was low. When the applied pressure was above 10 GPa, the absorption spectra of **SP-NO₂** showed a new peak at *ca.* 650 nm. During further compression process, the **SP-NO₂** crystals showed a gradual increase in absorbance. Even with the hydrostatic pressure was released, the newly emerged peak still existed, yet blue-shifted to 580 nm with the pressure gradually returned to ambient pressure (Fig. S1). The spectra under atmospheric pressure after pressure treatment (Fig. 1b) comported with that of **SP** after UV irradiation of Hg lamp at 365 nm for one hour under atmospheric pressure as a control experiment (Fig. S10), and the spectra reported for isomerization in PMMA matrix through UV irradiation³⁴. This result indicates the conversion to the **MC-NO₂** products after pressure treatment. The blue shift from 650 nm to 580 nm during the decompression process might be caused by the changes of electronic interaction between the compounds under high pressure^{36,37}.

To gain the visual information for the mechanochromism process, the images *in situ* for the **SP-NO₂** was taken and shown in Fig. 1c. During the compression process, the yellowish crystals started to darken and gradually turned into blackish red. Even after the complete discharge of pressure, the crystal retained the deep red colour. This phenomenon could be easily detected by naked eyes with no need of the excitation of UV light. In order to ensure the effect of pressure and exclude the influence of the external environment, the control experiment was conducted under a relative low pressure (0.9 GPa) and the UV-Vis spectra and the micrographs *in situ* were obtained at different time. The spectra changed minimally and the colour of the crystals remained the same (Fig. S11), which indicates that the isomerization of **SP-NO₂** came from the effect of high pressure rather than other factors.

To further understand the influence of pressure on the reaction, the kinetics and thermodynamics of the reaction were studied under different pressure through *in situ* UV-Vis spectroscopy. The absorbance of **MC-NO₂** at 650 nm was used as an index to monitor the isomerization of **SP**. Results showed that once pressure reached 10.0 GPa, the absorption spectra changed immediately and kept nearly the same even after holding for an hour, suggesting that the isomerization equilibrium to **MC-NO₂** had reached its equilibrium rapidly before the measurement. In the range of 10.0 to 15.0 GPa, at each holding pressure, the gradual increase of absorbance showed that more **MC-NO₂** was obtained under higher pressure and thus the compression process favoured the conversion to **MC-NO₂**.

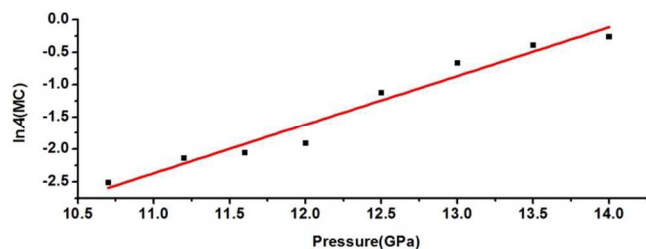


Fig. 2 Correlation of $\ln A(\text{MC})$ with pressure (P) in the pressure range of 10.0-14.0 GPa for **SP-NO₂**.

In order to quantify the relationship between the pressure and the reaction process, natural logarithm of absorbance ($\ln A(\text{MC})$) was plotted against pressure between 10.0 to 14.0 GPa (Fig. 2). It was found that the correlation was linear. The effect of pressure on chemical equilibrium could be described by the well-known relationship between pressure (P) and Gibbs' enthalpy of reaction³⁸,

$$\Delta V = \left(-\frac{\partial \Delta G}{\partial P}\right)_T = \left(-\frac{\partial \ln K}{\partial P}\right)_T RT \quad (1)$$

where ΔV is the volume of reaction³⁸, and K is equilibrium constant ($K = n(\text{MC}) / (n - n(\text{MC}))$). Due to the limited detection range of 10.0 to 14.0 GPa, $\ln[1/(n - n(\text{MC}))]$ can be approximated to be constant and $\ln K$ then to be proportional to the natural logarithm of percentage of **MC** form (see ESI), which can be indexed by absorbance $A(\text{MC})$. Thus, we can derive the following relationship:

$$\frac{\partial \ln A(\text{MC})}{\partial P} \propto \frac{\partial \ln K}{\partial P} = -\frac{\Delta V}{RT} \quad (2)$$

Therefore, it is not surprising to see the linear correlation of $\ln A(\text{MC})$ to P (Fig. 2) in the pressure range of 10.0 to 14.0 GPa. Accordingly, the positive slope of the linear region indicated a negative value for volume of reaction, in consistent with the observation that K increased with pressure. Although the correlation fitted well with the linear relationship and could be used as working curves in the range from 10.0 to 14.0 GPa, some factors must be considered in larger pressure region. For example, $\ln[1/(n - n(\text{MC}))]$ cannot be approximated to be constant, and the fluctuation of optical path length of the sample under high pressure must be taken into account. To quantitatively elucidate the mechanochromic behavior under pressure is important yet challenging³⁹, and is also our undergoing project.

To elucidate the generality of mechanochromic responses of **SPs**, two other molecules were tested for pressure-induced chromic responses. **SP-H** was chosen to give more insight on the effect of nitro- substituent group, while **SP-Ph** was the first reported photochromic **SP** that has been clearly described not to be photochromic in crystal^{27,40}. It was found that both **SP-H** (Fig. 3a) and **SP-Ph** (Fig. 3b) showed the visible mechanochromic responses *via* pressure-induced isomerization under high pressure. From the *in situ* UV-Vis spectroscopy, the correlation of $\ln A(\text{MC})$ with pressure fitted well with the linear relationship for both of them. However, unlike **SP-NO₂**, partial recoveries to **SP** form were observed after the release of pressure for **SP-H** (Fig. S4) and **SP-Ph** (Fig. S7). In general, for the isomerization from **MC** to **SP** form, the free volume to undergo ring closure was available during the decompression process. Nevertheless, the electron withdrawing group in **SP-NO₂** stabilized the **MC** form, thus suppressing the “reversed” isomerization. Another difference among these three compounds comes from the “threshold” pressure. During the compression process, **SP-H** showed obvious changes in UV-Vis spectra above 10.7 GPa, while **SP-Ph** showed changes under a relative lower pressure of 9.1 GPa. It indicates that **SP-Ph**, with a larger conjugate area, is more compressible and favourable to undergo the isomerization reaction. From these

data, it is reasonable to propose that the mechanochromic properties, such as “threshold” pressure, could be regulated through the structural modification of molecules *via* functional group substitution. In comparison with the benzoxazines having the similar pressure-induced responsive behavior in crystals⁹, spiropyrans have relative higher pressure threshold values and are easier to modify in structure.

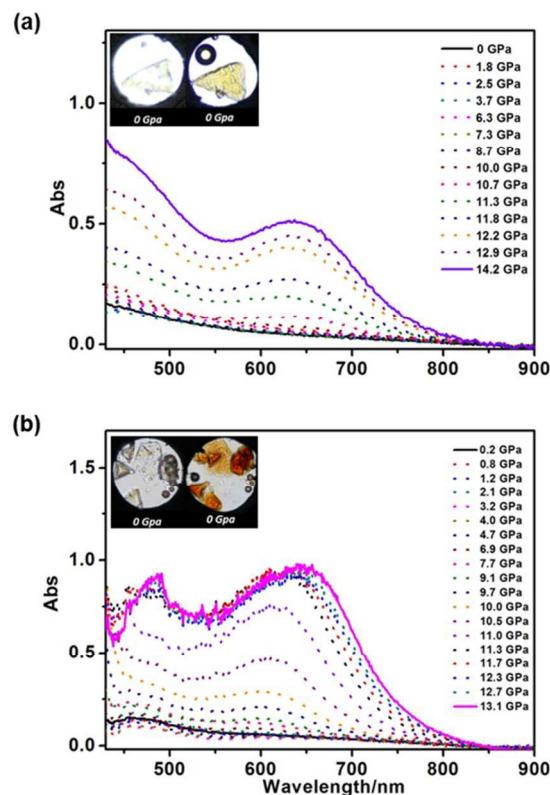


Fig. 3 *In situ* UV-Vis spectroscopy during the compression of (a) **SP-H** and (b) **SP-Ph** under different pressures. Micrographs *in situ* of the crystal before (left) and after (right) the pressure treatments are shown as inset.

From the crystal structure of **SP-NO₂** (Scheme 1b), spiroatom took the tetrahedron spatial configuration connected with four atoms. Due to the breakage of C-O bond during the isomerization, the hybridization of spiro carbon changed from sp^3 to sp^2 , and the transformations from spiro to more flexible and compressible planar structure were favoured under high pressure. These transformations also led to a negative volume of reaction accompanying with the ring opening. In addition, the mechanochromism of **SP** might also be influenced by the effective charge transfer process from the lone pair of the indoline nitrogen into the antibonding orbital of the C-O spiro bond^{41,42}. This interaction can be enhanced by the increased pressure, causing the pressure-induced planarization of **SP**⁴³. Besides, some other factors, such as the change of molecular energy under high pressure⁹ and crystal polymorphism, also should be considered in such mechanochromic process.

Conclusions

In summary, the visible mechanochromic isomerization process of **SP** was achieved by using the diamond anvil cells technique. Resulting from the negative volume of reaction, high pressure drives the isomerization equilibrium to favour **MC** form. The mechanochromic property of these compounds induced by high pressure could not only be applied in the design of novel sensing materials and pressure indicators, but also provide more insight into chemical reactions under extreme conditions.

This research was financially supported by the National Natural Science Foundation (No. 21074004, and 91227202) and the Ministry of Science and Technology (2013CB933501) of China.

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†Electronic Supplementary Information (ESI) available: experimental section, *in situ* UV-Vis spectra, derivation of equation and X-ray diffraction pattern. See DOI: 10.1039/c000000x/

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