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Visible responses under high pressure: phenolphthalein crystals and its analogues with adjustable ring-opening threshold pressures

Xinyuan Deng,<sup>a</sup> Hongwei Guo,<sup>b</sup> Xiao Meng,<sup>a</sup> Kai Wang,<sup>b</sup> Bo Zou<sup>\*b</sup> and Yuguo Ma<sup>\*a</sup>

The ring-opening reactions of phenolphthalein (PP) crystals under hydrostatic pressure provided by diamond anvil cell (DAC) is described in this paper for the first time. Color of the crystal changed into red from colorless visibly. The ring-opening threshold pressures could be adjusted by changing the substituent groups. The mechanochromic response under hydrostatic pressure could also be achieved in polymer blends, which contributes to the practical applications.

With real-time mechanical stimulus. responses to mechanochromic materials have attracted wide attention due to their potential applications in many fields, such as dynamic functional materials, memory devices, sensors, and logic gates.<sup>1</sup> Responses of reported mechanochromic systems are mostly triggered in solid state by grinding<sup>2</sup> or stretching<sup>3</sup>. In the condensed phase, the photophysical and mechanoresponsive properties of a given system is closely associated with the molecular aggregation state or stacking mode.2a-b,4 Thus an understanding of the relationship between mechanoresponsive properties and crystal structures is very important for the development of mechanochromic materials.<sup>5</sup> Compared with well understood pH-, light-, and temperature-sensitive materials, the studies on mechanism of mechanochromic materials remained inadequate, owing to the absence of effective quantitative tools for real-time and in situ investigation on the mechanochromic processes.

Pressure is an important thermodynamic parameter for chemical equilibria and chemical kinetics. Increases in pressure can reduce the volume available for the system.<sup>6</sup> Pressure as a common external stimulus can alter intermolecular

interactions<sup>7</sup> and even break the chemical bonds<sup>8</sup>. DAC techniques can provide isotropic high pressures<sup>9</sup> different from other anisotropic forces such as shearing or tension. When combined with spectroscopic measurements, DAC techniques offer a real-time and in situ investigation on the mechanochromic process and quantify the applied force.7 However, up to now, most of the reported mechanochromic systems are based on the changes of noncovalent interactions, molecular conformations and phase transitions, with small fluorescence shifts and reduced emission intensity.7,10 Mechanochromic materials based on chemical reactions have become more and more appealing due to their good color durability, no need of excitation light sources, and significant color transformations.<sup>11</sup> The mechanochromic materials based on the isomerization of spiropyrans and benzoxazines under hydrostatic pressure have been recently reported.<sup>11,12</sup> Since their ring-opening reactions could also be trigged by UV lights,<sup>13</sup> so their mechanochromic responses could be interfered by the UV lights.

We have studied the isomerization of spiropyrans under hydrostatic pressure.12 Decrease in volume resulted from ringopening reactions made it possible for spiropyrans to isomerize under high pressure. We concluded that change of hybridization of the spiro-carbon from sp<sup>3</sup> to sp<sup>2</sup> and subsequent planarization played important roles in the reduction of volume. On the track of such a lead, we would like to explore more practical mechanochromic system with the purpose of expanding their responsive pressure range. PP has structural features of a lactone and a twisted sp<sup>3</sup> carbon (Fig. 1). As a widely used pH indicator, its colorless lactone structure turns into red quinonoid structure via breaking the C-O bond under proper basic condition, with the sp<sup>3</sup> carbon changing to sp<sup>2</sup> carbon simultaneously.<sup>14</sup> PP was also extensively investigated in host-guest chemistry.<sup>15</sup> But the study of **PP** on mechanochemistry is rare. Only an early study in 1958 showed that PP experienced plastic deformation and ring-opening under shear stress provided by Bridgman anvils.<sup>16</sup> Different from shear stress, which induces homolytic cleavage of the C-C

<sup>&</sup>lt;sup>a.</sup> Beijing National Laboratory for Molecular Sciences, Center for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of Ministry of

Education, College of Chemistry, Peking University, Beijing 100871, China. E-mail: ygma@pku.edu.cn; Tel: +86-10-6275-6660 <sup>b.</sup>State Key Laboratory of Superhard Materials, College of Physics, Jilin University,

Changchun 130012, China. E-mail: zoubo@jlu.edu.cn

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backbone bonds of polymers,<sup>17</sup> hydrostatic pressure provides isotopic compression and static pressure.<sup>7a</sup> Here we report for the first time the mechanochromism of **PP** realized under hydrostatic pressure. The ring-opening of **PP** occurred when the pressure reached 7 GPa, different from 5 GPa for plastic deformation.<sup>16</sup> Besides, the stronger electron-donating effect of *N*,*N*-dimethylamino groups on **PP-NMe**<sub>2</sub> made its ringopening threshold pressure reduce to 5 GPa (Fig. 1), while **PP-H** had no response even when pressure reached 14 GPa, indicating a strong substitution effect. We further dispersed **PP-NMe**<sub>2</sub> into polymer matrix, and the blend showed mechanochromic response to high pressure.



**Fig.1** Relationship between electron-donating abilities of *p*-substituents with the ring-opening threshold pressures and absorption maxima of **PP** and its analogues **PP-NMe**<sub>2</sub> and **PP-H** under hydrostatic pressures.

The structure information provided by single crystal analysis facilitates better understanding of the mechanochromic properties of **PP**. The crystal data of **PP** retrieved from the Cambridge Crystallographic Data Centre (CCDC) show a lactone structure on the sp<sup>3</sup> carbon, and the molecule is twisty owing to the tetrahedral geometry of the sp<sup>3</sup> carbon (Fig. 2a). The lengths of C-O single bond in the lactone structure are 1.48 Å and 1.50 Å, which are longer than ordinary C-O bond length of 1.43 Å.<sup>18</sup> Twisty 3-dimensional structure of **PP** makes it easier to transform to planar structure under high pressure. Therefore, the ring-opening reaction which is resulted from the breakage of C-O bond in the lactone is likely to happen.

To test our hypothesis, **PP** crystals were investigated under pressure, and *in situ* UV-vis absorption spectroscopy was employed. When the applied pressure was low, absorbance in visible region increased slightly. When pressure reached 7 GPa, a new absorption band at ca. 530 nm was observed indicating the ring-opening of **PP**.<sup>11,12,15</sup> As pressure was further increased to 14 GPa, the emerging absorption band increased dramatically and the absorption maximum was red-shifted to ca. 550 nm. Increased absorbance under higher pressure suggested that more ring-opening products were present. That is, high pressure favours the ring-opening of **PP**. Correspondingly, *in*  During the decompression process, the emerging absorption peak was blue-shifted to 515 nm and decreased in intensity simultaneously (Fig. S2, ESI<sup>+</sup>). The red- or blue-shift of the absorption peak with increasing or decreasing pressure, were attributed to the changes of electronic interaction between the molecules.<sup>12,19</sup> Reduced absorbance suggested that the ringopening molecules transformed back to the ring closed forms.<sup>10a</sup> While the reverse reaction was not complete, according to the pale red crystal and absorption peak remained at 515 nm after the pressure released. Therefore, **PP** could be used as pressure sensor that keeps the mechanical history.

compression process. It could be observed by naked eyes.



 $\label{eq:Fig.2} \begin{array}{l} \textbf{PTP-MMe}_2 \ (c), \ (d)); \ \textbf{PP-H} \ ((e), \ (f)). \end{array}$ 

To further explore the effects of substituent groups on the ring-opening under pressure, PP-NMe<sub>2</sub> and PP-H (Fig. 1) were synthesized by substituting the hydroxyl groups on PP with N,Ndimethylamino groups and hydrogen atoms, respectively. Single crystals of PP-NMe<sub>2</sub> and PP-H were obtained via slow evaporations of solvents at room temperature. PP-NMe<sub>2</sub> also had visible mechanochromic response to pressure (Fig. 4). The crystal turned green from colorless during the compression process. A new absorption band was observed in the visible region when pressure reached 5 GPa. The absorption maximum remained at 650 nm after pressure was released (Fig. S4). Thus, the ring opening of **PP-NMe<sub>2</sub>** did occur under pressure. In contrast, for PP-H, the absorption spectra in visible region changed little even though pressure reached 14 GPa (Fig. S9, ESI<sup>+</sup>). The crystal remained colorless corresponding to the unchanged absorption spectra. Therefore, different ring-

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opening threshold pressures were obtained by changing substituent groups. Meanwhile, different color transformations were present and it provided visible correlation between responsive colors and applied pressure values. More importantly, UV lights could not trigger the ring opening of **PP** and its analogues (Fig. S1, ESI<sup>+</sup>). Therefore, they can be used as pressure sensors without the interference from the UV lights.



**Fig.3** (a) *In situ* UV-vis absorption spectra of **PP** under compression in the range of 0-14 GPa. (b) The comparison of UV-vis absorbance spectra of **PP** crystals before (0 GPa) and after (r-0 GPa) the pressure treatment. (c) Real optical images of a **PP** crystal in the compression and decompression processes.

*In situ* Raman spectroscopy was used to monitor the structure changes of the three molecules with increasing pressure (Fig. S6-8, ESI<sup>+</sup>). There were two relative strong Raman peaks around 770 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> of the three molecules assigned to ring C-H out of plane bending and ring C-C stretching, respectively.<sup>20</sup> As pressure was increased, the two Raman peaks shifted toward higher frequencies indicating that high pressure made the crystals more compact and strengthened the intermolecular interactions.<sup>21</sup> It echoed the red shift of absorption maxima in the compression processes. However, no obvious new peaks in Raman spectra of **PP** and **PP-NMe<sub>2</sub>** were observed, which probably was due to the low conversion of ring opening as well as the reduced signal-to-noise ratio as pressure increased.

In addition, the absorption spectra of **PP** (Fig. S3, ESI<sup>+</sup>) and **PP-NMe**<sub>2</sub> (Fig. S5, ESI<sup>+</sup>) under a fixed pressure changed little with prolonged time, indicating that ring-opening reactions reached equilibria rapidly after pressure was applied and that the responses originated from the stimulus of pressure. Quite different from stretching or shearing induced bond breakage in molecular switches, hydrostatic pressure leads to shrinkage in the volume of crystals. Thus, isomer occupying smaller volume is favoured under high pressure. According to the relationship between pressure and Gibbs' enthalpy of reaction as well as approximate low conversion, the correlation of ring-opening of absorbance A(**r-PP**), pressure *p* and volume change  $\Delta V$  is derived (ESI<sup>+</sup>):

$$\frac{\partial lnA(\boldsymbol{r}-\boldsymbol{P}\boldsymbol{P})}{\partial p} \propto -\frac{\Delta V}{RT}$$

Then the natural logarithm of absorbance (InA(**PP**)) at 533 nm was plotted with pressure from 7 GPa to 14 GPa (Fig. S12, ESI<sup>+</sup>).

It was found that slope of the correlation curve was positive. The same trend was obtained for **PP-NME**<sub>2</sub>(Fig.1913)(ESF))1146 positive slope indicated a negative value for the volume change in ring-opening reactions.<sup>12a</sup> High pressure favoured the ringopening product, which was compressible planar structure and occupied smaller volume. The slope was off a straight line in higher-pressure range probably for the higher conversion.



**Fig.4** (a) *In situ* UV-vis absorption spectra of **PP-NMe**<sub>2</sub> under compression in the range of 0-14 GPa. (b) Real optical images of a **PP-NMe**<sub>2</sub> crystal in the compression and decompression processes.

The ring-opening threshold pressures were 5 GPa for PP-NMe<sub>2</sub> and 7 GPa for PP, respectively. However, PP-H had no obvious mechanochromic response even at 14 GPa. From the crystal structure analysis of three molecules (Fig. 2), there are mainly intermolecular hydrogen bonding and CH/ $\pi$  interactions in the three crystals. We get the bond angles on the sp<sup>3</sup> carbon (Tab. S1, ESI<sup>+</sup>). Differences among the bond angle values for the three molecules are all less than four degrees, and most of them are less than one degree. It indicates the similar spatial configurations of the three molecules. Moreover, lengths of the three C-O bonds in the lactone are approximate each other. We believed that electronic effects of *p*-substitutions played an important role in different ring-opening threshold pressures. The electron-donating *p*-substituents could stabilize the carbocation to form more stable resonance structures.22 Therefore, smaller ring-opening threshold pressure was observed for PP-NMe<sub>2</sub> than that for PP. The fact that absorption maximum at 650 nm for PP-NMe2 was much more red-shifted than that at 515 nm for PP also demonstrated the stronger electron-donating effects of N,N-dimethylamino groups. As for PP-H, since hydrogen atom had no such electronic effects, no ring opening was observed even under 14 GPa.

When **PP-NMe**<sub>2</sub> (1 wt%) was dispersed in the commercial polymethyl methacrylate (PMMA), a visible color change was observed, and the threshold was 13 GPa (Fig. S11, ESI<sup>+</sup>). The absorption profile was similar to that in pure crystal. The mechanochromic threshold pressure was reduced to 11 GPa, when blend content of **PP-NMe**<sub>2</sub> was increased to 5 wt% (Fig. S10, ESI<sup>+</sup>). Elevating concentration of **PP-NMe**<sub>2</sub> could enhance signal-to-noise ratio in UV-vis absorption spectroscopy, thus

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lowering the responsive threshold pressures of polymer blends. It demonstrated an efficient way to prepare mechanochromic polymeric materials by blending mechanoresponsive organic molecules with commercial polymers.<sup>23</sup> Moreover, responding pressures could be adjusted by changing the concentration of organic molecules. The performance of polymer blends might facilitate their practical applications as pressure sensors.

In summary, a visible mechanochromic response of **PP** under hydrostatic pressure was achieved with the help of DAC techniques. **PP** could keep the mechanical history and had good color durability, which are important for pressure sensors. Furthermore, for the first time, different ring-opening threshold pressures and color change were obtained by changing substituent groups on the molecular structure. This can serve as an effective strategy to adjust the mechanochromic properties for other mechanochromic systems. **PP** and its analogues could expand the applied pressure range as mechanochromic sensors, and **PP-NMe**<sub>2</sub> can be used for pressure calibration being dispersed in polymer matrix. Most importantly, their ringopening reactions were inert to UV lights, so they were not interfered by UV lights in practical applications.

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The visible mechanochromism was triggered via the ring-opening reaction of phenolphthalein under high pressure. Different ring-opening threshold pressures and responsive colors were achieved by changing substituent groups with different electronic effects. Blend by dispersing the phenolphthalein analogue in PMMA demonstrate mechanochromic responses under pressure, which facilitated the practical applications as pressure sensors.