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Reversible piezochromism in a molecular wine-rack[†]

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The highly-polymorphic, strongly-coloured ‘ROY’ system exhibits a yellow→orange→red piezochromic response under hydrostatic compression. The ‘Y’ (yellow) polymorph accommodates the effect of pressure via a wine-rack-type mechanism, made accessible by the conformational flexibility of the molecule, all while retaining the crystal symmetry of the parent Y form. Decompression from 1.49 GPa demonstrates reversibility of this behaviour.

The ability to couple crystal colour/fluorescence to external pressure, as seen in piezochromic materials, is a highly-desirable feature for optical pressure-sensing devices.^{1–7} For such applications inorganic and organometallic complexes are usually favoured in preference to organic molecules — which are often colourless; although in some instances tuneable aromatic conjugation has led to strong colouration in organic systems.^{8–11} Most piezochromic responses in organics tend to occur on compression via grinding and then require heat or solvent exposure to reverse the colour transition;¹² examples of reversible colour tuning through application of hydrostatic pressure alone remain rare.^{3,13–17} Here we show how a simple supramolecular hinging mechanism can give rise to reversible piezochromism in an organic solid.

Pressure exerted by hydrostatic means can far exceed that of grinding (shear pressure) — the 0–10 GPa pressure range is readily achievable for organics.¹⁴ The advantage of applying large

pressures that do not damage the sample irreversibly (with respect to decompression) is that a much more pronounced change in crystal structure, and a potential piezochromic response, could result. In order to induce as strong a piezochromic response as possible in an organic system, we considered the flexibility afforded by both (i) the crystal lattice and (ii) the molecule itself. Among some of the most flexible inorganic systems are framework materials that distort under temperature or pressure through ‘mechanical’ means — low-energy hinging deformations seen in ‘wine-rack’ materials are a typical example of this.^{18–23} For example, hydrostatic compression of wine-rack topologies then results in negative linear compressibility (NLC), the phenomenon where one crystal dimension expands as the overall volume is reduced (see Fig. 1(b) in ref. 22). Only a handful of instances of this motif have been identified in molecular crystals, although its occurrence is probably under-reported.^{24–26}

Organic systems that pack with the wine-rack-type topology present appealing candidates for piezochromism whenever the ‘hinging’ mechanism can be coupled with tuneable optical properties. It is in this context that we chose to study 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile, or ‘ROY’ (Fig. 1(a)), so-named because of its extensive range of strongly-coloured red, orange and yellow polymorphs.^{27,28} Its colouration has been attributed predominantly to electronic interaction between the nitrophenyl and thiophenecarbonitrile moieties, mediated by the S–C–N–C dihedral angle θ (highlighted in Fig. 1(a)); thus the different crystal forms are considered conformational polymorphs.^{29,30} The molecular conformational dependence of the ROY polymorphs has made ROY a model system for exploring crystal structure prediction/conformational polymorphism analysis and controlled-crystallisation experiments.^{31–39}

Organic molecules are known to be resistant to the effects of pressure, relative to metal complexes, instead reducing their crystalline volume through reduction in intermolecular void space,⁴⁰ however they can exhibit modest flexibility in dihedral angles.⁴¹

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[†] Electronic Supplementary Information (ESI) available: CIFs of high-pressure structures, atomistic compression movie (QuickTime format), experimental details for high-pressure X-ray diffraction and UV–Vis absorption spectra measurements, photographs of ROY crystals, Gaussian fits to absorption spectra first derivatives, structure of the Y polymorph at 30 K and analysis of intermolecular interactions. See DOI: 10.1039/b000000x/

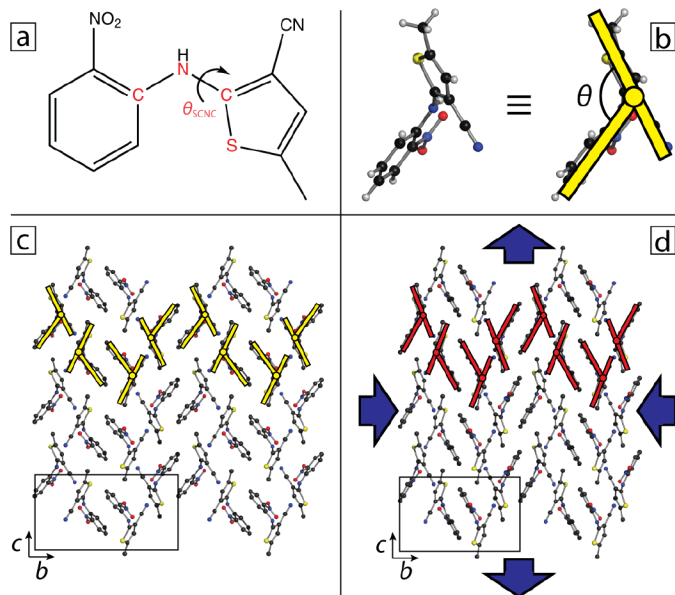


Fig. 1 (a) Molecular structure of ROY. The arrow indicates the main rotatable bond associated with crystal colour. (b) Diagrammatic representation of the ROY molecule as two rigid struts with a hinging node, approximately along the C–N bond. (c) Crystal packing of the Y form viewed along the *a*-axis under ambient conditions, and (d) at 5.2 GPa, where the blue arrows show directions of compression and expansion. Hydrogen atoms are omitted for clarity.

It is this conformational flexibility, coupled with a wine-rack topology, that we seek to exploit in ROY — where the rotatable bonds act as a molecular analogue to flexible metal ‘nodes’ in inorganic frameworks. Of the seven characterised ROY polymorphs, which are named after their colour and, sometimes, morphology, the yellow forms have near orthogonal alignment of their aromatic groups — $\theta = 112.8^\circ$ in the ‘YT04’ form — and the red forms adopt an approximately planar geometry, $\theta = 21.7^\circ$ in the ‘R’ form.²⁷ We chose to investigate the monoclinic, yellow ‘Y’ form (space group $P2_1/n$), anticipating that the effects of pressure would manifest in the form of ‘molecular flattening’, coupled with a wine-rack-type framework (shown in Fig. 1(b,c)), that would permit this deformation and ultimately drive a transformation to a redshifted crystal form.

Through collection of high-pressure X-ray single-crystal diffraction data to 5.2 GPa, using a Merrill-Bassett diamond anvil cell (DAC), we found that the Y form does indeed undergo a pronounced colour change but without proceeding via a phase transition; the crystal packing and symmetry remain unchanged and there are no volume discontinuities over the pressure range investigated.^{42,43} The crystal structure at 5.2 GPa is shown in Fig. 1(d). Fig. 2(a) shows the effect of pressure on the three orthogonal axes of the strain tensor ($\mathbf{X}_1 \equiv \mathbf{b}$; $\mathbf{X}_2 \approx 0.2\mathbf{c} - \mathbf{a}$; $\mathbf{X}_3 \approx -0.3\mathbf{a} - \mathbf{c}$) where the NLC response is evident along the \mathbf{X}_3 direction between 0.54 and 2.84 GPa: $K_I = -(\partial \ln I / \partial p)_T = -5.5(8) \text{ TPa}^{-1}$ over this pressure range. A refined third order Birch-Murnaghan equation of state, calculated using PASCAL, indicates the crystal is rather compressible, having a bulk modulus $B_0 = 6.0(7) \text{ GPa}$, up to 5.2 GPa, where $B' = dB/dp = 11.1(12)$.^{44,45} Consistent with the wine-rack

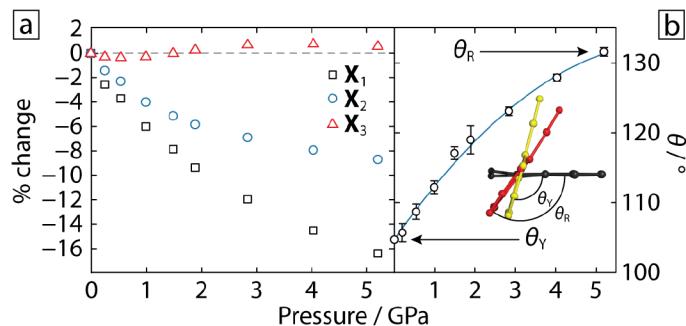


Fig. 2 (a) Effect of pressure on the three principal axes of the strain tensor. Standard deviations are within the size of the data points. (b) Change in dihedral angle θ (blue line: quadratic fit). Inset graphic: overlay of the ambient and high-pressure molecular structures, shown respectively by the yellow and red colours of the thiophenecarbonitrile groups. Nitrophenyl groups are shown in black.

motif, the \mathbf{X}_1 direction is the most amenable to pressure-induced change ($K_I = 29.4(8) \text{ TPa}^{-1}$) due to the prevalence of relatively compressible intermolecular π - π interactions aligned predominantly along this direction. This compression translates to a modest expansion along the perpendicular direction \mathbf{X}_3 . Experimental methods, CIFs, crystal structure refinement tables and lattice parameter/volume plots are available in the ESI†.

The mode of crystal structure compression can be traced to coupling between both the flexibility in the lattice, as described above, and the ROY molecule itself. The molecular dihedral angle θ becomes larger over the course of compression — $104.7(2)^\circ \rightarrow 131.6(6)^\circ$ — as the aromatic rings become increasingly coplanar (see Fig. 2(b)). That the θ angle becomes larger instead of smaller (*cf.* 21.7° in the R form) reveals that although the molecule flattens out — characteristic conformational geometry of the redshifted forms — the thiophenecarbonitrile group is actually rotated in the opposite direction relative to the nitrophenyl group, to any of the known orange/red forms, confirming rotational insensitivity identified in previous DFT predictions.⁴⁶ Diffraction measurements on a sample recovered from a DAC, post-exposure to 1.49 GPa, showed that the torsion angle and cell parameters revert to that of the pre-compressed ambient form (see ESI†).

The origin of the piezochromism has been discussed, so far, in terms of molecular conformation, however it is known that both intra- and intermolecular interactions can play a simultaneous role in influencing sample colour.⁴⁷ A discussion on the changes in intermolecular geometry is given in the ESI†, but in summary, we find that the colour change is most readily explained by the molecular conformation. Although it is possible that changes in aromatic $\pi \cdots \pi$ stacking distances — forming more evenly-spaced interactions — may make a limited contribution, there is no clear structure–colour relationship with respect to intermolecular interactions.

The change in crystal colour is evident microscopically, as shown in Fig. 3(a). In order to quantify the extent of colour variation, UV-Vis absorption spectra were measured for another Y-form crystal at pressures up to 3.01 GPa (Fig. 3(b)). The pressure dependence of the absorption edge increases from 495.6(7)

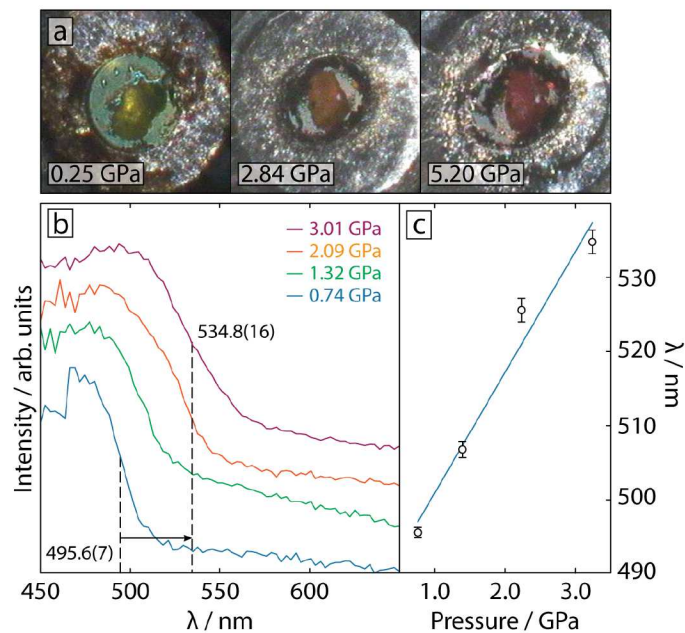


Fig. 3 (a) Pressure-induced colour change in a ROY single crystal. (b) UV-Vis absorption spectra with mid-points of leading absorption edges indicated in red. (c) Absorption edge dependence on pressure.

to 534.8(16) nm over the pressure range 0.8–3.0 GPa. The progression in colour change suggests an insensitivity to the relative directions in which the aromatic groups are rotated; it is only the degree of co-planarity that matters. Photographs of the crystal decompressed from 1.49 GPa show that the yellow colour returns, in accordance with the reestablishment of the ambient cell parameters and torsion angle (see ESI†). Crystal images for all pressure points, crystal structures, UV-Vis absorption experimental details and Gaussian fits are given in the ESI†.

The piezochromic behaviour seen here differs to most other organics in the sense that often it is most readily exploited by switching between two states that exist either side of a phase boundary, e.g. a single-crystal→single-crystal or single-crystal→powder transition, the latter achieved commonly through grinding.^{8,9} Here we have demonstrated the presence of appreciable visible colour change within a single phase; an overall shift in absorption of 39.2(17) nm up to 3.01 GPa. Extrapolation of the approximately linear dependence of absorption on pressure (see Fig. 3(c)) suggests a possible overall change in absorption of 80.69 nm by 5.20 GPa. This compares favourably to the magnitude of colour change seen in other hydrostatically-compressed systems: an absorption peak shift of 47 nm up to 6.56 GPa is seen in bianthrone; likewise a peak shift of ca. 40 nm over 6.3 GPa has been observed in some dithienylethenes (estimated from Fig. 10 in ref. 13), although a single-crystal phase transition occurs below this pressure.^{13,14} A boron-based benzothiazole-enamide compound showed an approximately linear shift in luminescence of 125 nm up to 10.34 GPa — implying a change of 62.5 nm by 5.17 GPa.¹⁷ Notable piezochromic responses have been seen in 9,10-bis((E)-2-(pyrid-4-yl)vinyl)anthracene, where fluorescence emission changes by as much as 127 nm at 5.45 GPa, and in tetrathiazoylthiophene where a shift of 53 nm occurs by

3.2 GPa.^{16,48}

Different applications of piezochromic materials demand colour-change functionality over varying ranges of pressure. Our key result here has been to show how molecular flexibility with a wine-rack topology can be used to produce a piezochromic response over a wide pressure range and the ROY system has the particular advantage that its piezochromism is reversible without requiring subsequent exposure to heat or solvent vapour. Furthermore its pronounced yellow→orange→red colour change is continuous in the absence of a crystallographic phase transition and is always visible to the naked eye, removing the need for spectroscopic measurement as might be required for visibly colourless crystals.

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