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Tuning the Mechanical Flexibility of Organic Molecular Crystal by Polymorphism for Flexible Optical Waveguide

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Abstract: The ability to selectively tune the optical and the mechanical properties of organic molecular crystals offers a promising approach towards developing flexible optical devices. These functional properties are sensitive to crystallographic packing features and are hence expected to vary with polymorphic modification. Using as a model system the photoluminescent material 4-bromo-6-[(6-chlorolpyridin-2-ylimino)methyl]phenol (CPMBP), we herein demonstrate the simultaneous tuning of mechanical flexibility and photoluminescence properties via polymorphism. Two new polymorphic forms of CPMBP were obtained from solution and fully characterised using a combination of experiment and density functional theory simulations. These polymorphic forms exhibit remarkably distinct mechanical properties and an order of magnitude difference in photoluminescence quantum yield. The mechanically plastic form has higher quantum yield than the brittle polymorphic form. However, the photoluminescence emission profile is largely unaffected by the observed polymorphism, thereby demonstrating that the optical properties and bulk mechanical properties can in principle be tuned independently. By distinguishing between material-light interactive and non-interactive light propagation, waveguiding properties of the plastic form of CPMBP (Form II) were explored using the straight and bent crystals to highlight the potential application of CPMBP in designing flexible optical devices. Our results demonstrated that polymorph engineering would be a promising avenue to achieve concurrent modulation of
Introduction

Soft amorphous materials such as organic polymers and elastomers have been studied extensively in academia and industry due to their high degree of mechanical adaptivity.\textsuperscript{1–5} In contrast, crystalline molecular materials are often brittle and prone to breaking upon external mechanical forces. This fragility of crystalline materials poses challenges for their application in next-generation technologies, including as sensors, synthetic tissues, and as advanced optoelectronics. Correspondingly, the recent discovery of mechanical flexibility in single crystals\textsuperscript{6} of molecular materials\textsuperscript{7–16} and coordination polymers\textsuperscript{17–20} opens new opportunities to design next-generation flexible technologies. Numerous applications of flexible molecular crystals have been already demonstrated including their use as optical waveguides,\textsuperscript{21–26} micro-optoelectronic devices,\textsuperscript{27,28} sensors,\textsuperscript{29,30} and biomimetics.\textsuperscript{31,32} While a growing number of mechanically flexible crystalline molecular materials are being reported, they remain scarce and their preparation is largely serendipitous.

Based on their qualitative mechanical behavior, flexibility of molecular crystals can be classified as plastically (irreversible) and elastically (reversible) bendable. Plastic bending in molecular crystals has been rationalized based on anisotropic molecular arrangements and the existence of facile slip planes where molecular layers interact via weak dispersive intermolecular interactions such as halogen bonding, $\pi\cdots\pi$ stacking, or weak van der Waals interactions.\textsuperscript{7,15} In contrast, elastic bending arises from energetically isotropic molecular packing with weak interactions.\textsuperscript{9,33} These weak interactions facilitate the displacement of molecules without disrupting the stabilizing forces that maintain the structural integrity of the crystal. The success of these structural criteria for elastic and plastic bending demonstrate that the bulk mechanical compliance of molecular materials is rooted in their crystal packing and non-covalent interactions (NCI).

The most obvious way to tune NCIs in crystalline materials is to modify the chemical functionality. This approach has been used widely in molecular and coordination polymers for altering the mechanical compliance.\textsuperscript{7,18,34} However, this approach is drastic and can change significantly the critical functional properties of the molecules. To overcome this limitation, crystal engineering strategies have been developed which allow to selectively tune NCIs by introducing multiple components in the crystal packing, cocrystallisation and salt formations.\textsuperscript{35–38} For example, Nath et al. recently reported how the plasticity of probenecid crystals could be
infused into brittle 4,4’-bipyridine via cocrystallisation. Although this crystal engineering approach does not require modification of the chemical functionality, the inclusion of multiple chemical entities into the material can impose restrictions of material compatibility. For example, where the material application requires biological or environmental compatibility, the inclusion of a toxic coformer would render the material unusable. To avoid any chemical modification whatsoever, NCIs can be tuned also by controlling polymorphism. Polymorphism stems from the ability of a molecule to crystallise in more than one solid form each having distinct arrangements or conformations of the constituent molecules. Tuning mechanical flexibility by controlling polymorphism of a molecular crystal of 6-chloro-2,4-dinitroaniline was first reported by Reddy and Desiraju in their pioneering work. More examples of tuning the mechanical response of molecular crystals through polymorph screening have been since reported.

The polymorphism of molecular crystals which show simultaneously mechanical flexibility and useful optical properties is rare. Single crystals of π-conjugated organic chromophores are frequently used as active micro-optical components such as optical waveguides, lasers, circuits, and field-effect transistors in designing advanced optoelectronic devices. However, these devices are predominantly prepared by using brittle forms of single crystals. By coupling mechanical flexibility to optical properties, a variety of optoelectronic applications can be envisioned. For example, by making use of elastically flexible materials, reversible optical sensors become feasible, whereas shapable nano-optical devices can be imaged through use of plastically bendable crystals.

In recent years, researchers have successfully identified mechanically flexible luminescent molecular materials. For examples significant efforts have been devoted to designing mechanically flexible optical waveguides. These materials have the properties of bending the path of light thereby offering potential applications in nano-optical devices. Similarly, various materials have been reported whose optical properties can be tuned by the extent of bending. More recently advanced optical properties have been also demonstrated to be tunable by mechanical bending including the polarization of plane polarized light. Thus, fine tuning the interplay between optical and mechanical properties has significant potential for next generation functional materials. Only recently has polymorphism been revealed as a potential design strategy for simultaneously modifying both the optical and mechanical properties of molecular crystals. Although the strategy seems promising only limited number of examples have been reported. Further studies are required to explore the breadth of this phenomenon before its full potential can be realized.
Polymorphism in molecular crystals is ubiquitous.\textsuperscript{40} For the purpose of the study, we opt to explore the polymorphism of 4-bromo-6-[(6-chloropyridin-2-ylimino)methyl]phenol (CPMBP). This molecule was selected as salicylaldehyde-derived Schiff bases are well known to be highly photoluminescent and often show polymorphism in solid-state.\textsuperscript{52} Moreover, the chlorine and the bromine atom on the backbone of the molecule can be expected to introduce mechanical compliance in crystal forms. This molecule has significant potential for studying simultaneous effect of polymorphism on the optical and mechanical properties.

**Experimental**

**Materials**

2-Amino-6-chloropyridine (98%; CAS No: 45644-21-1) and 5-bromosalicylaldehyde (98%; CAS No: 1761-61-1) were purchased from Fluorochem and AlfaAesar respectively and used as received.

**Synthesis and Crystal Growth**

2-((E)-(6-chloropyridin-2-ylimino)methyl)-4-bromophenol (CPMBP) was synthesised by liquid assisted mechanochemical grinding (LAG) with methanol (50 $\mu$L) of an equimolecular mixture of 5-bromosalicylaldehyde (201 mg, 1 mmol) and 2-amino-6-chloropyridine (129 mg, 1 mmol) with a mortar and pestle using 100 $\mu$L of methanol. Single crystals were grown by dissolving the ground powder in DCM, followed by slow evaporation or anti-solvent crystallization in a beaker or tube.

**Powder X-ray Diffraction (PXRD)**

The grounded crystals were packed into borosilicate capillaries (inner diameter 0.5 mm). PXRD data were collected on a Bruker D8 Discover diffractometer (Bruker AXS, Karlsruhe, Germany) equipped with a LYNXEYE XE detector and Cu-K\textalpha\, radiation ($\lambda = 1.506 \, \text{Å}$). Data were collected from $2\theta = 3^\circ$ to $50^\circ$ with a step size of 0.009$^\circ$ and 6 s/step.

**Single-Crystal X-ray Diffraction**

Single crystal X-ray diffraction (SCXRD) data of both polymorphs were collected using a Bruker D8 Venture diffractometer (Bruker AXS, Karlsruhe, Germany) equipped with graphite-monochromated Mo K\textalpha\, radiation ($\lambda = 0.71073 \, \text{Å}$). Data reduction was performed using the Bruker AXS SAINT$^{53}$ and SADABS\textsuperscript{54} software packages. Both structures were solved by SHELXT 2018$^{55}$ using Direct Methods, followed by successive Fourier and difference Fourier syntheses. Full-matrix least-squares refinements were done on F\textsuperscript{2} using SHELXL 2018$^{56}$,
including anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms bonded to oxygen were located from the electron density maps, and all hydrogen atoms bonded directly to carbon atoms were fixed at their ideal positions. Data collection, structure refinement parameters, and crystallographic data of the cocrystals are summarized in Table S1.

**Differential scanning calorimetry (DSC)**

Differential scanning calorimetry (DSC) measurements were performed with a TGA/DSC 3+ (Mettler Toledo, Greifensee, Switzerland). Measurements were performed in open aluminum crucibles under continuous N₂-air flow. The experiments were conducted at a heating rate of 10 K/min over a range of 25 °C to 550 °C.

**Fourier-Transform Infrared Spectroscopy (FTIR)**

FTIR spectra for powdered samples were measured using a Nicolet FT-IR NEXUS (Thermo Fischer, Dreieich, Germany) spectrometer equipped with a Diamond-ATR-Golden Gate unit and a DTGS KBr detector. Each spectrum was collected across a range of 200–4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹.

**Photoluminescence Spectroscopy**

Photoluminescence measurements were performed with an Edinburgh Instruments (Livingston, UK) FLS 980 fluorescence spectrometer. All photoluminescence spectra were measured in an integrating sphere. The samples were excited with a 450-W ozone-free xenon arc lamp. The detector was a R928P PMT, electrically cooled to -20 °C.

**Waveguide**

The use of CPMBP as a waveguide material was tested by using LED light sources (Thorlabs Inc.). For the measurement the light was coupled into the CPMBP waveguides placed on a silicon wafer with a 3 µm thick SiO₂ layer with a microscope objective (100x magnification, 0.8 numeric aperture (NA), Nikon Inc) using the end-fire coupling method. Coupling the light in the direction of the waveguide optical axis facilitates the investigation of propagation behavior. At the other end of the crystal the outcoupled light was collected perpendicular to the optical axis of the waveguide by applying another objective (10x magnification, 0.25 numeric aperture). The collected light was subsequently guided via fibers to a CCD detector (Kymera 328i, Oxford instruments Inc.). Since CPMBP shows photoluminescence, we differentiate between active and passive waveguiding. Active waveguiding describes the propagation of the emitted light caused by the photoluminescence provided the wavelength of
the LED source is in the excitation range. The light propagation without any interaction is denoted as passive waveguiding. A schematic picture of the measurement setup can be found in the Supporting Information Scheme S1.

Computational methods

Initial structures were taken from experimentally determined single crystal X-ray diffraction data, as described above. Plane wave density functional theory (pw-DFT) calculations were performed using Quantum ESPRESSO v6.4.\textsuperscript{57,58} Structure relaxation was performed using the Generalized Gradient Approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE)\textsuperscript{59} with the exchange-dipole moment (XDM)\textsuperscript{60} dispersion correction. The nuclear-electron interactions were approximated using the projector augmented-wave method,\textsuperscript{61} and the electronic wave function was expanded in plane waves to a kinetic energy cut-off of 80 Ry. Convergence of the electronic wave function was accepted <10\textsuperscript{-10} Ry, and forces were considered as converged when <10\textsuperscript{-5} Ry/a.u. The Brillouin zone was sampled on a Monkhorst–Pack grid\textsuperscript{62} with 0.06 Å\textsuperscript{-1} for Form I and 0.05 Å\textsuperscript{-1} for Form II, respectively.

Intermolecular interaction energies were calculated using the CLP-PIXEL method,\textsuperscript{63,64} and associated wrapper MrPIXEL,\textsuperscript{65} using a condensation level of 4 and cluster radius 15 Å. PIXEL calculations were based on \textit{ab initio} charge densities (grid size 0.06 Å) produced at the B3LYP/6-31G(d,p) level of theory within Gaussian v16,\textsuperscript{66} with hydrogen positions normalized to conventional neutron data.

Results and Discussion

The compound, CPMBP was synthesized by liquid assisted mechanochemical grinding (LAG) with methanol of an equimolecular mixture of 5-bromosalicylaldehyde and 2-amino-6-chloropyridine, Fig. 1a. Slow evaporation of a saturated CH\textsubscript{2}Cl\textsubscript{2} solution of CPMBP at room temperature in a beaker yielded flake-shaped orange crystals. When crystals were handled with a metal needle, some crystals displayed brittle nature and others showed plastic bending and remained deformed even after removal of the stress, Fig 1b-c, suggesting concomitant formation of two polymorphic forms. In contrast, crystallization of CPMBP in pure DCM or using an anti-solvent in glass tubes produced pure mechanically distinct flake-shaped crystals, presumably owing to the different crystallisation kinetics as compared with crystallisation from a wide-mouthed beaker. Crystals obtained from DCM with n-hexane were brittle (Form I) over both the long crystallographic faces. In contrast, crystals obtained from pure DCM deformed plastically (Form II) over the major faces but appeared brittle over the other faces. Powders of
each of the pure crystal forms exhibited a single endothermic peak in their differential scanning calorimetric profiles, corresponding to their melting (Fig. S1): 153.8 °C and 158.0 °C for Form I and Form II, respectively. The phase purity is also consistent with the unique PXRD diffraction pattern of the powders of the crystals (as compared with simulated PXRD from single crystal data, Fig. S2) and FT-IR spectra (Fig. S3). The FT-IR spectra of the two polymorphs are nearly identical. For example, the aromatic C-Br stretching vibration in both forms is at 1072 cm\(^{-1}\). The C-H deformation vibration of the 2,6-substituted pyridines is also at the same position, 792 and 730 cm\(^{-1}\), respectively.\(^{67}\)

**Fig. 1** (a) Chemical structure of title compound, CPMBP. (b, c) Optical images depicting brittle and plastic deformation behaviour of Form I and Form II, respectively.

To understand the intermolecular interactions and molecular packing motifs responsible for the observed distinct mechanical flexibility of two different crystalline forms of CPMBP, the crystal structures of both forms were determined by SCXRD. Form I (brittle) crystallizes in the orthorhombic space group \(Pca_2_1\) with one CPMBP molecule in the asymmetric unit. The cell parameters are \(a = 25.13\) Å, \(b = 3.87\) Å, \(c = 11.98\) Å (Table S1). The CPMBP molecules adopt a near-planer conformation with a dihedral angle of 8.4° between the pyridyl and phenolic rings, driven by the intramolecular O-H\(\cdots\)N hydrogen bonds (Fig. S4a; H\(\cdots\)A: 1.86 Å, \(\theta: 146.1°\)). Crystal face indexing by SCXRD indicates that the two long crystallographic faces are the (001)/(00\(\overline{1}\)) and (010)/(0\(\overline{1}\)0), whereas (100)/(1\(\overline{0}\)0) are the top faces (Fig. 2a and Fig. S5a). In the crystal structure, each molecule is connected to two other molecules via C-H\(\cdots\)O (2.62 Å, 147.8°) and C-H\(\cdots\)Cl (2.89 Å, 146°) interactions to form a corrugated ribbon (Fig. 2b). The molecules in the ribbon are slip stacked along the crystallographic \(b\)-axis via \(\pi\cdots\pi\) interactions (3.87 Å), which are further stabilized via C-H\(\cdots\)Br (2.95 Å, 148°) interactions (Fig. 2c). The ribbons are connected via C-Cl\(\cdots\)\(\pi\) interactions along the crystallographic \(a\)-axis. Together these interactions lead to the formation of a mechanically interlocked 3D network structure.
preventing the molecules from moving in response to mechanical stress (Fig. 2d). Hence, the crystal structure is consistent with the observed brittle fracture (Fig. 2e and Fig. S6a).16,44

![Fig. 2 Molecular packing in the crystal structure of Form I of CPMBP. (a) Schematic diagram of crystal face indices determined by single-crystal X-ray diffraction. (b) 1D ribbon is formed via C–H⋯O, C–H⋯Cl, C–H⋯Br interactions along c-axis (C–H⋯O interactions: red dotted lines, O–H⋯N interactions: cyan dotted lines and C–H⋯Cl interactions: orange dotted lines and C–H⋯Br interactions: green dotted lines). (c) Slip-stacked arrangement of CPMBP molecules along the [010] direction through π⋯π interactions. (d) Mechanically interlocked 3D network structure along the [010] plane. The blue arrow indicates the direction in which the mechanical force was applied during bending. (e) Optical microscopic photographs of brittle fracture during three-point bending experiment of single crystals of Form I.](image)

Form II (plastic) crystallizes in monoclinic space group \( P2_1/c \) with cell parameters \( a = 4.44 \, \text{Å}, b = 19.01 \, \text{Å}, c = 13.90 \, \text{Å}, \beta = 90.18^\circ \) (Table S1). Like in Form I, there is also one CPMBP molecule in the asymmetric unit that adopts a near-planar conformation with dihedral angle between the pyridyl and phenolic rings is of 3.3° due to the intramolecular O-H⋯N hydrogen bonds (Fig. S4b; H⋯A: 1.85 Å, θ: 146.2°). The two larger faces of crystals of Form II are the (010)/(0\overline{1}0) and (001)/(00\overline{1}) faces, with the minor face being (100)/(\overline{1}00) (Fig. 3a and Fig S5b). In the crystal structure, the molecules are connected to dimers by C-H⋯O (2.64 Å, 148.4°)
bonds (Fig. 3b). These dimers are slip stacked via \( \pi \cdots \pi \) interactions (3.3 Å) along the growth axis of the crystal (\( a \)-axis) to construct a columnar assembly (Fig. 3c). These stacked columns close-pack in the orthogonal direction (\( b \)-axis) through weak hydrophobic –C\(_2\) groups (Fig. 3d). This feature provides slip planes or weak interaction planes along the [001] direction. The structure of Form II is overall anisotropic with low energy slip planes, which is the conventional crystal engineering criterion for plastic bending (Fig. 3e and Fig. S6b). Thus, upon mechanical stress perpendicular to the slip planes, (010) face results plastic deformation in crystal of Form II. These low energy slip-planes may also contribute to the formation of extended defects which can influence mechanical properties.68,69

**Fig. 3** Crystal packing of Form II of CPMBP. (a) Schematic diagram of crystal face indices determined by single-crystal X-ray diffraction. (b) Dimers are formed via C–H⋯O interactions along \( c \)-axis (C–H⋯O interactions: red dotted lines and O–H⋯N interactions: cyan dotted lines). (c) Slip-stacked arrangement of CPMBP molecules along the [001] direction through \( \pi \cdots \pi \) interactions. (d) Molecular packing with slip planes along the (001) plane (cyan dotted lines). The blue arrow shows the direction in which the mechanical force is applied during bending. (e) Optical microscopic photographs of plastic bending upon mechanical stress along the (010) plane of the single crystals of Form II.

The intermolecular interactions in both polymorphs were investigated via Hirshfeld surface analysis using Crystal Explorer 17.5.70 The contribution from all interactions in both the polymorphs are depicted in Fig. S7, which reveals higher number of specific interactions in Form I. Quantitative analysis of the intermolecular interactions in both polymorphic forms was
obtained using the Coulomb-London-Pauli (CLP) PIXEL method for energy decomposition from quantum mechanical charge densities.\textsuperscript{53,64} This method has been widely applied to the study of intermolecular interactions in molecular solids.\textsuperscript{71–73} In brittle Form I, the strongest interactions are those formed by $\pi\cdots\pi$ interactions along the $b$-axis (-37.9 kJ.mol\(^{-1}\)). In contrast, the crystallographic $c$-axis (dominated by C-H\cdots O, C-H\cdots Cl, and C-H\cdots Br interactions) averages ca -27.5 kJ.mol\(^{-1}\), with the crystallographic $a$-axis (comprising no specific interactions) being much weaker at ca. -7.8 kJ.mol\(^{-1}\). Consistent with prevailing design strategies for molecular flexibility, the intermolecular interaction energies for the plastic Form II are more anisotropic than for Form I. The $\pi\cdots\pi$ interactions are somewhat stronger (-40.7 kJ.mol\(^{-1}\)), reflecting the shorter interplanar spacing along the $\pi$ stacked axis. Interactions along the $c$-axis axis (C-H\cdots O interactions) are again stronger, -21.8 kJ.mol\(^{-1}\), with the $b$-axis C-H\cdots $\pi$ interactions having energies of ca. -12.8 kJ.mol\(^{-1}\).

\textbf{Fig 4:} Intermolecular interaction energies for (a) Form I and (b) Form II. All energies are described between the element-coloured molecule (denoted grey in legend) in the centre, and its coloured pair, as indicated in the legend. Full energy decomposition tables are provided in ESI Tables S2-S4.

Following from the interesting effects of polymorphism on the mechanical properties, we sought to explore whether the polymorphism also affected the optical properties. To collect the solid-state photoluminescence spectra (PL), the PL excitation (PLE) spectrum for each polymorph was first measured, Fig. S8. The respective maximum of each PLE spectrum was used as the excitation wavelength for the PL emission measurements. Both crystalline forms of CPMBP exhibited different emission properties, presumably owing to their distinct intermolecular interactions and molecular packing in the solid-state, Fig. 5. A powdered sample
of Form I exhibited very weak orange emission at 605 nm ($\lambda_{ex} = 425$ nm; $\Phi = 0.4$ %) compared to powdered Form II, which showed bright yellow emission at 585 nm ($\lambda_{ex} = 425$ nm; $\Phi = 8.7$ %). The band gap for both Forms is bound by predominantly carbon-based $2p_z$ states (see Fig. 6 and Fig. S9-S10). We can therefore suggest that the red-shift of the Form I emission spectrum (as compared with Form II) presumably stems from its weaker $\pi-\pi$ stacking interactions (see Figure 4).

**Fig. 5** Solid-state photoluminescence spectra of the brittle (Form I, black line) and plastic (Form II, red line) forms of CPMBP ($\lambda_{ex} = 425$ nm).

The photoluminescence quantum yield, 

$$\Phi_{PL} = \frac{k_r}{k_r + k_{nr}}$$

depends on the relative rate of radiative $k_r$ and non-radiative $k_{nr}$ decay. In a crystal, the latter is dominated by emission of high-order phonons. As the vibrational spectra of both polymorphic forms are nearly identical, Fig. S3, we do not expect significant difference in the non-radiative decay pathways between the polymorphic forms. We instead sought a qualitative rationale for the expected quantum yields by considering the differences in radiative decay rates. For solids, $k_r$ depends on whether the band gap is direct or indirect, and on the probability of emission (here limited to spontaneous emission within the weak coupling regime). The band gaps calculated under periodic conditions at the PBE-XDM level (see Fig. 6), are 1.82 eV for Form I (compared with experimental 2.05 eV optical gap) and 1.85 eV for Form II (compared with experimental 2.12 eV optical gap). Thus, our simulations are consistent with
Fig. 6 Selected areas of the band structure and Density of states (DOS) of (a) Form I and (b) Form II. The black line shows the total DOS and the red line represents the DOS projected onto C-based atomic 2$p_z$ orbitals. The blue arrow indicates the conduction band and the green arrow the valence band. The complete band structure is provided in the ESI, Fig S8 and S9.
experimentally observed trends in the photoluminescence emission wavelengths for both polymorphs, albeit with the expected underestimation from the use of a GGA functional. However, no indications for significant difference in the momentum transfer across the band gap were observed.

Under the highly idealized assumption that dipolar coupling is conserved in both polymorphic forms, decay can be roughly approximated with the number of available states in the conduction band (ε_f) and the number of states in the valence band (ε_i) via
\[ k_r \propto \int d\mathbf{k} \delta(\epsilon_f(\mathbf{k}) - \epsilon_i(\mathbf{k}) + \hbar\omega) \]
where \(\hbar\omega\) is the photon energy. Integrating over the corresponding states for each polymorphic Form (see Fig. 6) we observe \( k_r(\text{Form II}) > k_r(\text{Form I}) \), consistent with experimental observation. Hence, stemming largely from carbon-based 2pz states this further suggests that the different optical properties in the crystals stem from their unique \(\pi...\pi\) interactions.

**Waveguiding Properties**

To test CPMBP single crystals as potential optical waveguides, incident light was focused through a microscope objective onto the (100) face of the crystals, Fig. 7. Emitted light was subsequently collected perpendicular to the optical axis of the waveguide. Two different LED photon sources were considered for incident light; a 455 nm source was used to test active transport (i.e. where absorption and re-emission are possible) while a 730 nm source was used to test for passive transport (i.e. where absorption is not possible), Figs. 7b-c. In both cases, guided light was observed to leak through defects along the crystal.

When using the 455 nm incident source, the emission spectrum collected at end of the crystal was very similar to the conventional solid-state PL spectrum, (see Fig 7d and Fig. 5). However, the high energy part of the guided emission spectrum is filtered out due to the self-absorption of the CPMBP crystal. The ability of CPMBP to absorb its own photoluminescence on account of a small Stokes shift suggests it may be a promising candidate as a flexible wavelength-division multiplexing material. This effect will be the focus of follow-up investigation. In contrast, the guided emission spectrum from the 730 nm incident source is unaffected by the crystal, Fig 7d. The whole spectra of the used LED light sources, PLE and PL can be found in the supporting information Fig. S11 (455 nm) and Fig. S12 (730 nm).
Fig. 7 a) Optical microscope image of a Form II straight crystal placed on a silicon wafer with a 3 µm thick SiO$_2$ layer as in Scheme S1 b) light with 455 nm was coupled at the left end of the crystal c) light with 730 nm was coupled at the left end of the crystal d) detected PL-spectra at the right end of the crystal. LED light source, PLE and PL spectra are given in Figs. S11 and Fig. S12.

To observe the effect of plastic bending on the waveguiding properties of Form II CPMBP guided emission spectra from both 455 nm and 730 nm incident sources were again measured on the bent single crystals, Fig. 8. As compared with the straight crystals of Form II (Fig 7) no difference in shape or intensity of the emission spectra at either incident energy was observed. This suggests Form II CPMBP conserves its waveguiding functionality upon deformation.

Fig. 8 Optical microscope images of (a) bent crystal placed on a silicon wafer with a 3 µm thick oxide layer, (b) light with 455 nm was coupled at the left end of the crystal (c) light with 730
nm was coupled at the left end of the crystal (d) detected PL-spectra at the right end of the crystal.

The promising optical behavior of CPMBP single crystals suggests significant technological potential. The combination of self-absorption and flexibility can be exploited to simplify the light coupling into micron-scaled waveguide systems.\textsuperscript{27,28} Since the CPMBP molecules form single crystals, it can be assumed that the structure affects the polarization of the propagating light. These characteristics of the CPMBP waveguide crystal can be applied in photonic systems for specific usages, which makes the CPMBP molecule an interesting material regarding to photonic circuits.

Conclusions

We report here two polymorphic forms of a photoluminescent, 4-bromo-6-[(6-chlorolpyridin-2-ylimino)methyl]phenol with distinctly different optical and mechanical behaviors. The two polymorphs show similar morphology and colour and could be obtained as pure forms by controlled crystallization using different solvent mixtures. Form I adopts a mechanically interlocked 3D network structure with various weak non-covalent interactions. In contrast, Form II exhibits anisotropic crystal packing with low energy slip planes. Hence, Form I was found to be mechanically brittle, whereas Form II showed plastic deformation upon mechanical stress. Photoluminescence spectroscopy revealed that brittle Form I is only weakly emissive whereas the emission of plastically flexible Form II is comparatively bright. Only a minor red shift of the emission spectrum of Form I is observed as compared with Form II, which can be correlated with the stronger $\pi$-$\pi$ stacking interactions in the crystal packing of Form I. Moreover, due to the presence of shapable plastic flexibility combined with bright luminescent properties, Form II exhibits the properties of bending the path of light, i.e., flexible optical waveguide. Both active and passive waveguiding were observed. We therefore demonstrate how the mechanical properties of organic lumiphores can be tuned by controlling polymorphism instead of chemical modification. We expect polymorph engineering to become an important direction for designing mechanically flexible crystals with multifunctional application in flexible optoelectronics.
Scheme 1. Schematic representation of the polymorphic engineering mechanically flexible optical materials. The mechanochemical pictogram is take from ref.\textsuperscript{77}

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Form I: Brittle

Weak Emission

Form II: Plastic

Strong Emission

Flexible Optical Waveguiding