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Optical Waveguiding Organic Single Crystals Exhibiting Physical and Chemical Bending Features

Zhuoqun Lu, Yuping Zhang, Hao Liu, Kaiqi, Ye, Wentao Liu, and Hongyu Zhang*

Abstract: Bendable (elastic and plastic) organic single crystals have been widely studied as emerging flexible materials with highly ordered packing structures. However, even though manifold bendable organic crystals have been recently reported, most of them only display bending ability under the single circumstance. Herein, we report an organic single crystal of (*Z*)-4-(1-cyano-2-(4-(dimethylamino)phenyl)vinyl)benzonitrile, which could bend under external stress (physical process) or in the hydrochloric acid atmosphere (chemical process). This observation indicates that multiple crystal bending modes might be achieved in the same single organic crystal by simultaneously optimizing the structure at both molecular and supramolecular levels. Furthermore, the crystal exhibits bright orange-yellow emission and possesses good property of active low-loss optical waveguide in both the straight and the bent state, which indicates a potential optical application.

The study of the mechanical properties of organic crystals has become a burgeoning orientation in crystal engineering for its potential application in various fields.[1–4] Recently, the research of elastic organic single crystals (EOSCs) has become a cutting-edge field because EOSCs tend to be applied in flexible devices which is a focus in the development of current advanced material and technologies.[5–8] Ghosh and Reddy are precursors in the study of EOSCs and proposed mature mechanisms.[9,10] Then Koizumi and his coworkers firstly reported an elastic π-conjugated molecule 1,4-bis[2-(4-methylthienyl)]-2,3,5,6-tetrafluorobenzene with intense fluorescence.[11] Based on these findings, many EOSCs were reported constantly and further potential applications were developed successively in recent years. Our latest research gave a direction for realizing active optical waveguides in the elastically bent crystals, which developed an important optical application of organic crystals. We designed elastic crystals of Schiff base and derivatives of single-benzene compounds, which exhibit excellent properties of flexible optical waveguide and even amplified spontaneous emission.[12–16] The flexibility of crystals thrives the research topics in crystal engineering. Nevertheless, in addition to physical stress, some other inducements like heat, solvent, and irradiation also result in the deformation of crystals, which were seriatim reported in the past decade. Naumov and coworkers reported the spatial photocontrol over the optical output from slender single crystals of an azo compound.[17] Hu and his coworkers designed a solvatomechanical cocrystal of perylene and TCNB which responses mechanically to THF solvent.[18] Zhang reported a self-healing cocrystal of coronene and TCNB that bends and splits when the crystal is heated and restores to initial state after cooling.[19] All these works have revealed the diversity of inducements. Hence, it is significant to realize the

assembly of different stimuli-response mechanical properties, which is also instructive to the exploitation of new versatile organic solid materials.[20,21] Although different bending forms of organic crystals have been developed, few of these masterpieces about organic crystals have accomplished the combination of different mechanical stimuli-responses.[22] Therefore, there emerges a new challenge to the extension of multiple stimuli-responsive bending organic crystals with optical applications. However, it is very difficult to achieve the combination of multiple mechanical properties. On the one hand, it is quite tough to build the rational construction of molecular structure and predict the packing modes of crystals, which characterizes crystals with bending ability and luminescence. On the other hand, some special substituents that can alter the molecular configuration under special conditions need to be introduced in proper position and have to be impervious to packing modes of crystals. Therefore, perfect compatibility should be carefully considered in the design of multiple stimuli-responsive organic bending crystals.

Based on this situation, herein we report a dual stimuli-responsive bendable organic luminescent crystal of (Z)-4-(1-cyano-2-(4-(dimethylamino)phenyl)vinyl)benzonitrile CN-DPVB (Figure 1a). The high-quality needle-like single crystals with lengths in centimeter scale are elastically bendable under external applied stress and exhibit bright orange emission with a quantum yield of 0.19 (Figure 1b–d). Cyan and dimethyl amino substituted on both ends of the π-conjugated framework facilitate a donor-acceptor structure that favors luminescence.[23] Weak intermolecular interactions such as π-π stacking account for its mechanical bendability. Besides, dimethyl amino is a common substituent that is prone to get protonation and thus is more likely to alter the molecular structure. Therefore, it was observed that the CN-DPVB could bend automatically under the hydrochloric acid atmosphere, which has been not reported yet (Figure 1e). Meanwhile, CN-DPVB crystals also display quite good active optical waveguide in both the straight and the bent state. This new accomplishment of bendable crystals may particularly enrich the diversity of organic functional materials.
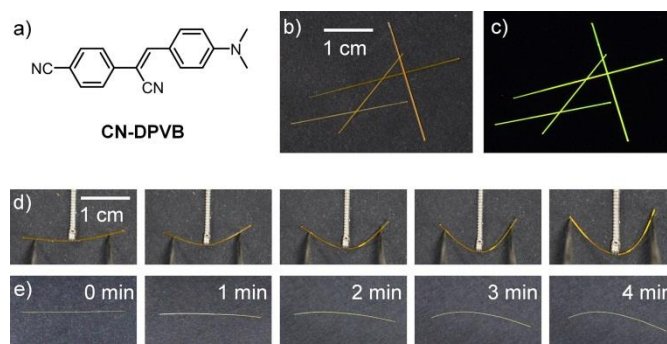

Figure 1. a) Molecule Structure of CN-DPVB. Photograph of the needle-like single crystals of CN-DPVB taken under room light b) and 365 nm UV light c). d) Physical bending under external stress applied through a pair of tweezers. e) Chemical bending process under the hydrochloric acid atmosphere.

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When a CN-DPVB crystal was applied with external stress, it was easily bent into an arc of almost 180° (Figure 1d) without rupture and restored instantaneously upon the withdrawal of force. And the bending-relaxing process could repeat reversibly for many times. The single crystal structure of CN-DPVB was determined for a further investigation of the observed elasticity. CN-DPVB crystallizes in monoclinic space group P2$_1$/c with one molecule in an asymmetric unit (Figure S1). Individual molecules connect via two kinds of C–H···N interaction (N···H distance between cyan and dimethyl amino: 2.599 Å, distance between C and N: 3.504 Å. N···H distance between cyan and benzene: 2.627 Å, distance between C and N: 3.338 Å). Two benzene rings in one molecule twist about 8° in a *trans* conformation across the C=C bond. Thus the whole molecule is relatively planar, which conduces to the intermolecular π-π stacking. The bendable face is determined in the morphology calculation of CN-DPVB by Material Studio 8.0. Based on the calculation, (001) plane is the widest and bendable plane of crystal that grows along *a* axis. Moreover, the morphology of the crystal was characterized to be an oblique hexagonal prism (Figure S2), which almost corresponded to the observation by microscope. The molecular arrangements in different directions are shown in Figure 2a. Molecules form two subtle π-π interactions of cyan-benzene (3.447 Å) and dimethyl amino-benzene (3.560 Å) in each line which connects reciprocally via C–H···N interaction (N···H distance: 2.599 Å,) finally generating a layer structure of molecules (Figure 2b). Each layer is perpendicular to the (001) plane and connects via C–H···N interaction. When the crystal is applied with external stress, a far-range movement of parallel molecules is prohibited because of the crisscrossing packing mode observed along the plane (10-3) (Figure 2c) but a subtle motion from the equilibrium position is allowed. Meanwhile, the weak interactions of C–H···N and C–H···C are prone to rupture and restore and therefore absorbs and releases the strain energy during the entire bending process. When a crystal is applied with stress, the distance between molecules increases in the outer arc to disperse the external stress energy and molecules in the inner arc become more contracted to each other due to the compression (Figure 2b). However, the whole structure and energy equilibrium will be destroyed when external stress exceeds the threshold limit, eventually leading to the crystal fracture. Three-point bending test was carried out to measure the modulus (E) of CN-DPVB crystals, which is an important index for the evaluation of elasticity (Figures 3 and S3). The linear curve of stress and strain validates the elasticity of CN-DPVB, which also indicates that there is no plasticity exhibiting in the whole bending process (Figure 3a). Modulus E is the quotient of the stress (σ) and the strain (ε) which were calculated according to the derived formulas (Figure S4).[24] The average value of elasticity modulus is calculated to be 0.905 GPa, indicating a quite good elastic bending ability of CN-DPVB crystals.

In addition to the external stress mechanical response, CN-DPVB crystal also exhibits a bending feature when it was exposed to a stream of HCl vapor dried by bubbling through concentrated sulfuric acid. The mechanical property of a fumed crystal CN-DPVB@HCl was tested and confirmed to be brittle and could not be deformed (Figure S5). As shown in Figure 1e, one single crystal that absorbed concentrated hydrochloric acid formed a fumed crystal CN-DPVB@HCl. The crystal began to bend slowly after two minutes accompanied by color fading.[25,26] Then the crystal was kept in HCl vapor for 12 h to ensure the complete reaction with HCl. Eventually, the crystal could not

become straight. It was observed that the surface of the crystal got rough and lost transparency after exposure to HCl in the SEM image (Figure S6), which indicated that the transformation was not single-crystal to single-crystal. Different from the physical stress, this process is irreversible and the bent crystal could not restore to its initial state by alkali flow or heat. Apart from hydrochloric acid, a sequel of volatile acids such as formic acid, acetic acid, propionic acid and trifluoroacetic acid (TFA) were also tested. Whereas crystals were found to dissolve in the TFA and there was no other emergence of crystal bending phenomenon in other acids, which showed a selectivity of hydrochloric acid. In addition, different faces of crystal were respectively fumed by HCl acid to find the bendable planes in this process. Surprisingly, it was found that the widest face (001) plane was the bendable plane under the hydrochloric acid stimulation, which resembled the situation of physical stress. Moreover, the fluorescence of the entire crystal faded as the process progressed.[27,28]
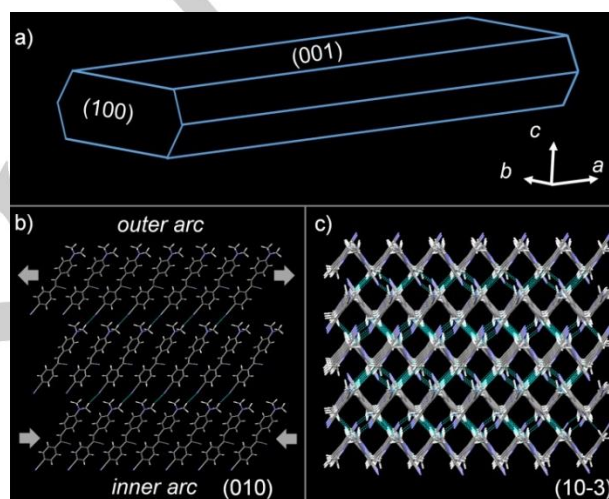

Figure 2. a) The growth morphology of CN-DPVB crystal calculated by Material Studio 8.0 and its crystal indices. b) The molecular arrangement of (001) plane observed along a axis. c) The molecular arrangement observed along (10-3) plane.

For a further investigation, single crystals of CN-DPVB hydrochloride (CN-DPVB·HCl) were attained by recrystallization of CN-DPVB in acetone with an extra addition of a small amount of concentrated hydrochloric acid (Supporting Information). CN-DPVB·HCl were light yellow blocks and crystallize in the triclinic space group P-1 with one molecule in an asymmetric unit (Figure S7 and S8). Proton NMR tests for CN-DPVB, CN-DPVB·HCl, and CN-DPVB@HCl crystals were carried out (Figure 3b and 3c). The peak's shapes of three crystals were almost the same but chemical shifts differed a little from each other. Peaks of the fumed crystals CN-DPVB@HCl moved to the low field and those of two hydrogens on the benzene which is closest to nitrogen atom shifted obviously (from 6.72 and 6.74 to 7.71 and 7.31 ppm, respectively). Lower shielding factor caused by the diminishing electron density of molecules is the reason for the low-field motion. When nitrogen atoms get positively charged by protonation, its electronegativity increased and was more likely to attract electrons and then resulted in the decrease of electron density and shielding factor. The chemical yield of salt formation in the crystals was 18-35% which was determined by weight changes (Table S1). Meanwhile, Raman spectroscopy test was also carried out (Figure S9). The peak of 1370 cm^{-1} corresponding to the stretching vibration of C-N in the dimethyl amino decreased conspicuously after the process.[29]

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Furthermore, we attempted to analyze the crystal structure after fuming but failed to obtain the crystal structure of the fumed crystal. The fumed crystals CN-DPVB@HCl tended to be brittle, exacerbating over time in the hydrochloric acid atmosphere, which suggested a devastation of crystal structure. XRD studies of initial crystals and fumed crystals were carried out to inspect the fuming degree. In comparison, the XRD pattern of fumed crystal was similar to the CN-DPVB but some new peaks appeared (Figure S10 and S11). The result suggested that this bending process was not a complete phase transformation. The fumed crystal still possessed the crystal structure as CN-DPVB crystal. Combing the results of XRD and NMR experiments, we could conclude that the fumed crystal CN-DPVB@HCl was a mixture of CN-DPVB crystal and its hydrochloride CN-DPVB·HCl. It basically maintained the crystal structure of CN-DPVB but partially altered the molecular configuration to the hydrochloride CN-DPVB·HCl. Hence, the crystal structure of CN-DPVB·HCl could provide important information to explain the bending mechanism of this unusual hydrochloric acid atmosphere induced crystal bending.
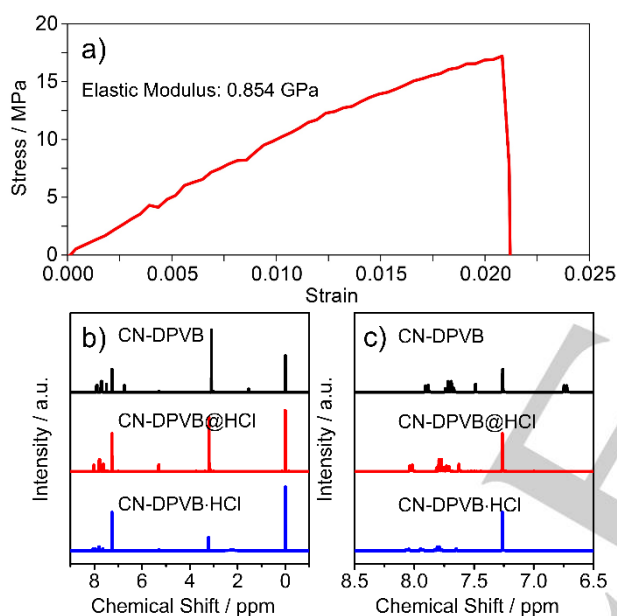

Figure 3. a) Load-displacement curves of CN-DPVB single crystal. b) Comparison of NMR spectrum between CN-DPVB, CN-DPVB@HCl and CN-DPVB·HCl. c) Amplified NMR spectrums between 6.5–8.5 ppm.

In the crystal of CN-DPVB·HCl, chlorine atoms occupy all vertexes of one cell and one chlorine atom forms an ion bond with a nitrogen cation (4.180 Å) which leads to a 70° rotation of dimethyl amino group. Two benzene rings in one CN-DPVB·HCl molecule twist about 24.41°, greatly larger than the angle of 7.56° in CN-DPVB molecule (Figure S12). Moreover, as shown in Figure 4b and 4d, the distance between the dimethyl amino of two adjacent molecules increases from 3.56 Å to 4.61 Å. This situation may be the critic factor for the chemical HCl induced bending process. During the fuming process, we took a video (Supporting Information) to record the variation of crystal fluorescence under UV light. It was found that the fluorescence of both sections disappeared initially, suggesting the protonation beginning on two sections of the crystal (Figure 4e).

When crystals were fumed, drastic rotation of dimethyl amino would lead to an increase of the distance between adjacent CN-DPVB molecules due to the insufficient space. Moreover, space occupation of chlorine atoms in the crystal also contributes to

the subtle motion of protonated molecules. Both the drastic rotation of dimethyl amino in the CN-DPVB molecules and the space occupation of chlorine atoms enlarge the distance of protonated molecules, which leads to the deformation of the crystal structure. Therefore, a probable mechanism of the acid-induced bendability is proposed as follows: when a single crystal was fumed with hydrochloric acid, molecules on both sections would initially get protonated accompanied with the drastic rotation of dimethyl amino groups. Adjacent molecules expanded on account of the deficient space between them and then resulted in the deformation of partial crystal structure, which accumulated with the process and eventually became strong enough to bend the crystal. Because the degree of deformation was relevant to the number of molecules that got protonated, the largest plane of crystal containing the most molecules was capable of bending in comparison with other faces.
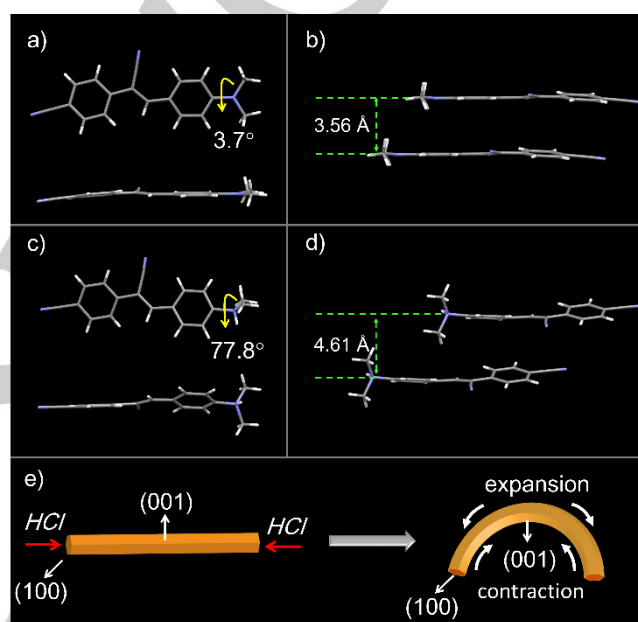

Figure 4. a) Conformation of single crystal CN-DPVB. b) Distance between the dimethyl amino of two adjacent molecules in CN-DPVB. c) Conformation of CN-DPVB·HCl single crystal. d) Distance between the dimethyl amino of two adjacent molecules of hydrochloride CN-DPVB·HCl. e) Schematic diagram of the bending process in hydrochloric acid atmosphere.

In contrast with two different bending modes, they resemble each other in the principle of bending but differ from the approaches. In both forms, a portion of molecules in the crystal deviate slightly from their equilibrium position. The microscopic subtle alteration eventually magnifies to the macroscopic deformation of crystal. However, they are disparate when it comes to the approach of alteration. Physical strain merely breaks the weak intermolecular interactions that could restore easily. Thus, it is a reversible process. On the contrary, chemical reaction completely alters the molecular structure and its configuration. Therefore, the acid-stimuli bending process is irreversible and destructive to crystal structure. On the other hand, the chemical process is much slower than the physical process. The microscopic force needs to accumulate as the reaction proceeds until it is strong enough to generate a deformation on two sections. Hence, the physical process is instantaneous but the chemical process is time-consuming.

In addition to the study of mechanical properties of CN-DPVB crystal, its potential optical application was also exploited in both the straight and the bent state. The emission (558 nm) and lifetimes (2.69 ns) in the straight and the bent state were

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unchanged due to the subtle alteration of molecular interactions in the bending process. This consequence encouraged us to investigate the optical waveguide performance of CN-DPVB crystal in the straight and the bent state. When different positions of straight CN-DPVB crystals were irradiated by a pulse laser, the emissions generating at one end were recorded (Figure 5a and 5c). According to the graph, emission intensities gradually enhance with diminishing the distances between recorded end and irradiated position. Based on fitting the collected data of Figure 5c, according to the literature,[30] optical loss coefficient (OLCs) at 558 nm was evaluated be 0.358 dB•mm^{-1} (Figure S13), which is relatively small among the reported organic crystals and polymers (Table S2), indicating a promising good optical property. The identical crystal was bent and adhered to a glass slide with glue (Figure 5b). After implementing the same optical waveguide measurements, it has realized flexible optical waveguide of CN-DPVB crystal in the bent state. Notably, the OLCs of bent CN-DPVB crystal at 558 nm was evaluated to be 0.409 dB•mm^{-1} (Figure S13), which was only 0.051 dB•mm^{-1} larger than the result determined in the straight state. Therefore, it is corroborated that the optical propagation is not influenced in the bent crystals. Furthermore, the optical waveguide property could switch off upon detection of HCl, which acts as a potential chemical sensor (Figure S14). Moreover, it was discovered that the CN-DPVB@HCl could not exhibit the ability of passive waveguide, which ascribed to the defects generated in the protonation.
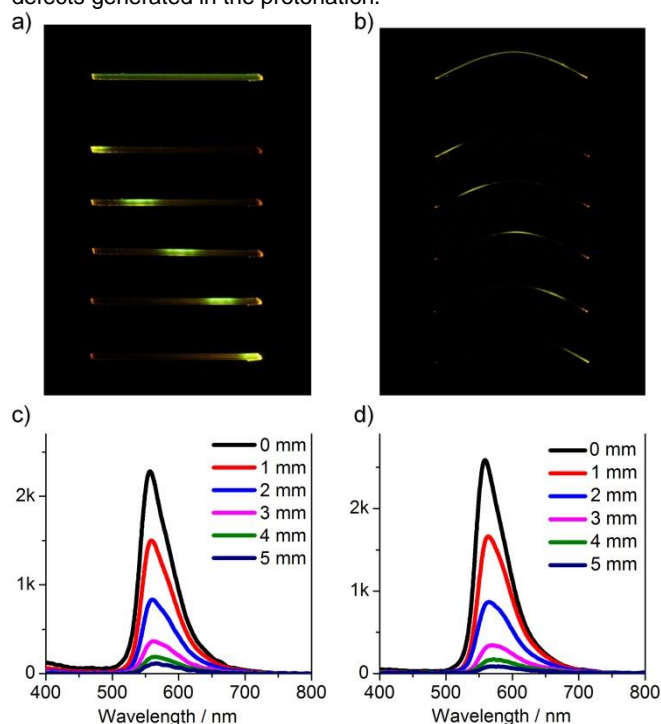

Figure 5. a) Straight crystal and b) bent crystal excited with a UV lamp (uppermost line) and with 355 nm laser focused at different positions. Fluorescence spectra collected at a tip of a single CN-DPVB crystal in the c) straight state and d) bent state with the distance between this tip and the excitation site of the laser changed gradually.

In conclusion, we reported an orange-yellow emissive organic crystal that exhibits dual bending features in the physical and chemical process. The crystal possesses good elastic property under the physical stress and bends conspicuously under the hydrochloric acid atmosphere. Moreover, low-loss optical waveguide was realized in both the straight and the bent crystals, which indicates a potential optical application. Two different bending manifestations reveal the possibility of developing multi-bending responsive organic crystals. By rational modification of molecular structures and substituents, more different types of multiple mechanical-responsive organic crystals will be developed and may further extend their application in manifold fields.

Acknowledgements

[1] S. Varughese, M. S. Kiran, U. Ramamurty, G. R. Desiraju, *Angew. Chem. Int. Ed.* **2013**, *52*, 2701–2712.
[2] S. H. Mir, Y. Takasaki, E. R. Engel, S. Takamizawa, *Angew. Chem. Int. Ed.* **2017**, *56*, 15882–15885.
[3] S. Takamizawa, Y. Takasaki, T. Sasaki, N. Ozaki, *Nat. Commun.* **2018**, *9*, 3984.
[4] S. Saha, M. K. Mishra, C. M. Reddy, G. R. Desiraju, *Acc. Chem. Res.* **2018**, *51*, 2957–2967.
[5] L. Catalano, D. P. Karothu, S. Schramm, E. Ahmed, R. Rezgui, T. J. Barber, A. Famulari, P. Naumov, *Angew. Chem. Int. Ed.* **2018**, *57*, 17254–17258.
[6] Y. T. Zheng, H. Sato, P. Y. Wu, H. J. Jeon, R. Matsuda, S. Kitagawa, *Nat. Commun.* **2017**, *8*, 100.
[7] S. Ghosh, M. K. Mishra, S. B. Kadambi, U. Ramamurty, G. R. Desiraju, *Angew. Chem. Int. Ed.* **2015**, *54*, 2674–2678.
[8] E. Ahmed, D. P. Karothu, P. Naumov, *Angew. Chem. Int. Ed.* **2018**, *57*, 8837–8846.
[9] S. Ghosh, C. M. Reddy, *Angew. Chem. Int. Ed.* **2012**, *51*, 10319–10323.
[10] S. Ghosh, M. K. Mishra, S. Ganguly, G. R. Desiraju, *J. Am. Chem. Soc.* **2015**, *137*, 9912–9921.
[11] S. Hayashi, T. Koizumi, *Angew. Chem. Int. Ed.* **2016**, *55*, 2701–2704.
[12] H. P. Liu, Z. Q. Lu, Z. L. Zhang, Y. Wang, H. Y. Zhang, *Angew. Chem. Int. Ed.* **2018**, *57*, 8448–8452.
[13] R. Huang, C. G. Wang, Y. Wang, H. Y. Zhang, *Adv. Mater.* **2018**, *30*, 1800814.
[14] B. Liu, Q. Di, W. T. Liu, C. G. Wang, Y. Wang, H. Y. Zhang, *J. Phys. Chem. Lett.* **2019**, *10*, 1437–1442.
[15] H. Liu, K. Ye, Z. L. Zhang, H. Y. Zhang, *Angew. Chem. Int. Ed.* **2019**, *58*, 19081–19086.
[16] R. Huang, B. Tang, K. Ye, C. Wang, H.Y. Zhang, *Adv. Opt. Mater.* **2019**, 1900927.
[17] J. M. Halabi, E. Ahmed, L. Catalano, D. P. Karothu, R. Rezgui, P. Naumov, *J. Am. Chem. Soc.* **2019**, *141*, 14966–14970.
[18] Y. Q. Sun, Y. L. Lei, H. L. Dong, Y. G. Zhen, W. P. Hu, *J. Am. Chem. Soc.* **2018**, *140*, 6186–6189.
[19] G. F. Liu, J. Liu, X. Ye, L. N. Nie, P. Y. Gu, X. T. Tao, Q. C. Zhang, *Angew. Chem. Int. Ed.* **2017**, *56*, 198–202.
[20] S. Hayashi, S. Y. Yamamoto, D. Takeuchi, Y. Ie, K. Takagi, *Angew. Chem. Int. Ed.* **2018**, *57*, 17002–17008.
[21] T. Takeda, M. Ozawa, T. Akutagawa, *Angew. Chem. Int. Ed.* **2019**, *58*, 10345–10352.
[22] P. Gupta, D. P. Karothu, E. Ahmed, P. Naumov, N. K. Nath, *Angew. Chem. Int. Ed.* **2018**, *57*, 8498–8502.
[23] X. Cheng, K. Wang, Huang. S, H. Y. Zhang, H. Y. Zhang, Y. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 8369–8373.
[24] A. Worthy, A. Grosjean, M. C. Pfrunder, Y. N. Xu, C.Yan, G. Edwards, J. K. Clegg, J. C. McMurtrie, *Nat. Chem.* **2018**, *10*, 65–69.
[25] Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, *Chem. Soc. Rev.* **2012**, *41*, 3878–3896.
[26] W. Fang, Y. Zhang, G. Zhang, L. Kong, L. Yang, J. Yang, *CrystEngComm*, **2017**, *19*, 1294–1303.
[27] X. Cheng, D. Li, Z. Zhang, H. Zhang, Y. Wang, *Org. Lett.* **2014**, *16*,

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880–883.

[28]   P. Pragyan, K. Virendra, W. MD., P. Abhijit, *ACS Appl Mater. Interface* **2018**, *10*, 44696–44705.

[29]   J. Laska, R. Girault, S. Quillard, G. Louarn, A. Pron, S. Lefrant, *Synthetic Met.* **1995**, *75*, 69–74.

[30]   Y. Li, Z. Y. Ma, A. S. Li, W. Q. Xu, Y. C. Wang, H. Jiang, K. Wang, Y. S. Zhao, X. R. Jia, *ACS Appl. Mater. Interfaces* **2017**, *9*, 8910–8918.

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Optical Waveguiding Organic Single Crystals Exhibiting Physical and Chemical Bending Features

Functionalized bendable organic crystals: Organic crystals of a benzonitrile derivate in centimetre size have been readily prepared and exhibit bright yellow emission. These crystals display physical and chemical bending features, which achieved the combination of multiple bending modes in one single crystal. In addition, the elastic crystal shows waveguiding property in the straight and highly bended state, indicating its application in flexible optical devices.