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- Authors: Rajadurai Chandrasekar, Mari Annadhasan, Abhijeet R. Agrawal, Surojit Bhunia, Vuppu Vinay Pradeep, Sanjio S. Zade, and Chilla Malla Reddy

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Mechanophotonics: Flexible Single-Crystal Organic Waveguides and Circuits

Mari Annadhasan,^{[a],§} Abhijeet R. Agrawal,^{[b],§} Surojit Bhunia,^[b] Vuppu Vinay Pradeep,^[a] Sanjio S. Zade,^{[b],*} C. Malla Reddy,^{[b],*} and Rajadurai Chandrasekar^{[a],*}

 [a] Dr. M. Annadhasan, V. V. Pradeep, Prof. R. Chandrasekar Functional Molecular Nano/Micro Solids Laboratory School of Chemistry, University of Hyderabad Prof. C. R. Rao Road, Gachibowli, Hyderabad 500 046, Telangana, India E-mail: r.chandrasekar@uohyd.ac.in
 [b] A. R. Agrawal, S. Bhunia, Prof. S. S. Zade, Prof. C. M. Reddy

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER), Kolkata, Mohanpur, West Bengal, 741246, India E-mail: sanjiozade@gmail.com; cmallareddy@gmail.com

§ These authors contributed equally to this work.

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Abstract: Microfabrication of circuits by combining the mechanical and photonic properties of flexible crystals is imperative for flexible miniature photonic devices. The fundamental understanding of molecular packing and energetics of intermolecular interactions is vital to design crystals with intrinsic flexibility and optical attributes. We present a unique one-dimensional optical waveguiding crystal of dithieno[3,2-a:2',3'-c]phenazine (1) with high aspect ratio displaying high mechanical flexibility and selective self-absorbance of the blue part of its fluorescence (FL). Though, macrocrystals exhibit elasticity, microcrystals deposited at a glass surface behave incredibly like plastic crystals due to significant surface adherence energy, making them suitable for constructing photonic circuits via micromechanical operation with atomic force microscopy cantilever tip. Phenomenally, the flexible crystalline waveguides display optical path-dependent FL signals at the output termini in both straight and bend configuration suitable for wavelength division multiplexing technologies. A futuristic reconfigurable 2×2 directional coupler fabricated via micromanipulation by combining two arc-shaped crystals split the optical signal via evanescent coupling and deliver the signals at two output terminals with different split ratios. The presented mechanical micromanipulation technique could also be effectively extended to any flexible crystals to design and carve complex photonic circuits.

Crystals are usually brittle and inelastic.^[1] Most of the crystalbased devices which employ active micro-optical components such as optical waveguides,^[2] cavities,^[3] lasers,^[4] circuits,^[5] and field-effect transistors^[6] are all finished in rigid platforms. On the contrary, the next-generation "smart" technologies demand flexible devices with the forecasted market of USD 70 billion by 2026.^[7] Flexible devices require mechanically reconfigurable crystals as active microcomponents. Flexible crystals are quite rare. Therefore, the quest for such crystals with unusual mechanical properties, for instance, elasticity (reversible deformation) and plasticity (irreversible deformation) has recently arisen to exploit them^[8-10] for smart flexible device technologies. The few known examples of millimetre-sized crystals demonstrated their flexibility upon manipulation with sharp mechanical objects.^[8] Crystals possessing interlocked host structure, weak and dispersive interactions and mobile solvent channels with the ability to store elastic energy generally show reversible deformation in response to external mechanical stress.^[1,8] Some of the millimetre-long flexible crystals also



Scheme 1. Cartoon representation of a 2×2 directional coupler constructed from two flexible organic crystals via mechanical micromanipulation with AFM cantilever tip. The molecular movements at (011) plane during bending is shown at the bottom right corner.

performed as optical waveguides in straight and bent geometries.^[9] The use of flexible crystal waveguides in photonic micro-circuits is limited by lack of suitable manipulation technique to morph microcrystal(s) into intricate shapes. Further, the implementation of mechanical operation in microcrystals is rather tricky due to their soft and fragile nature. Micromanipulation with atomic force microscopy (AFM) cantilever tip has turned out to be a promising technique^[11] to mechanical shaping of microcrystals without causing damage to them.

Enabling multidirectional optical communications requires crystal waveguides generating and transducing light signals of different wavelengths, a technique called wavelength-division multiplexing (WDM). Production of crystal waveguides with high flexibility and WDM property is a challenging task. Use of flexible microcrystals, possessing self-absorbance of part of fluorescence (FL) is a promising approach to realise mechanically compliant WDM crystal waveguides and microphotonic circuits. However, to the best of our knowledge, exploitation of flexible WDM microcrystals to construct mechanically reconfigurable waveguides and photonic circuits has not been realized yet.

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Figure 1. (a) Molecular structure of dithieno[3,2-a:2',3'-c]phenazine 1. (b) Schematic of the morphology of the crystal. (c) Images (video-grabs) showing elastic bending of a single crystal: 1-3) first bending cycle under applied mechanical stress using a forceps (on the left) and a metal needle (on the right). 4-6) the subsequent shape recovery of crystal upon stress withdrawal. (d) Representative load-depth (*P*-*h*) curve corresponding to quantitative data obtained by nanoindentation perpendicular to (01-1) face at 1 mN peak load.

Here, for the first time, we report the rare mechano-photonic attributes, viz., mechanical flexibility coupled with WDM in singlecrystals of dithieno[3,2-a:2',3'-c]phenazine (1) (Figure 1a). We demonstrate, (i) structural basis for the extraordinary crystal flexibility, (ii) mechanical compliance of crystals of 1 for bending under micromanipulation conditions with AFM cantilever tip and (iii) mechanical assembly of two arc-shaped waveguides forming a 2×2 directional coupler^[12] with two inputs and outputs, which could split the transducing optical signals and deliver at two different outputs with different split ratios (Scheme 1).

Synthesis procedure for compound 1 is provided in supporting information (Scheme S1). Compound 1, which is an important class of polycyclic conjugated molecule, was characterized by various techniques, including the fluorescence (FL) spectroscopy. The FL quantum yield of compound 1 in dichloromethane solution was found to be 14% which was calculated with respect to quinine sulfate as reference (see Supporting Information). Pale-yellow crystals of 1 were obtained from dichloromethane solution with a hexane layer on top (see Supporting Information). The macro-crystals could be bent into a loop without breaking in a three-point bending test by applying mechanical stress with a pair of forceps and a needle (Figure 1c, labels 1-3 and video S1, in Supporting Information). Upon release of the stress, the crystals restored to original shape on their own and did not show any sign of permanent damage (or strain), hence are elastic in nature with excellent mechanical flexibility (Figure 1c, labels 4-6).^[8] The crystals break when bent into smaller loops. For instance, a crystal with a thickness of ~20 μm broke when the diameter of the loop was decreased to around 0.8 mm (Supporting Information, Figure S1 and Video S2). The maximum strain the bent crystals could withstand was in the range of 2.5-2.8%. This is comparable to the strain in known elastically bendable molecular crystals.^[8] We further quantitatively measured the mechanical properties of the crystals using nanoindentation technique.^[13c] Indentation tests were performed on (01-1) face of the crystal with 0.2 mN/sec loading rate using a peak load of 1 mN. The corresponding load (P) vs displacement (h) curves are shown in Figure 1d). The extracted elastic modulus (E) and hardness values (H) are 5.83 ± 0.62 GPa and 0.26 ± 0.01 GPa, (Figure 1d) in the loading region indicate sudden displacement of the indenter tip at constant load. Literature



Figure 2. Crystal packing and elastic bending mechanism of **1**. (a) ORTEP diagram (with 50 % probability) and packing viewed along [100] and [011], showing stacking and herringbone arrangement. (b) Plausible mechanism of elastic bending involving elongation (left) and compression (right) of outer and inner arcs, respectively, along the length of the bent crystal. Notice the orientation of molecules on the outer (away from planarity) and inner arcs (towards the planarity of herringbone structure). The molecules shown in grey shade in the packing diagrams (a, bottom-left) and (b) are from a row below and overlap with weak interaction plane of top layer, making permanent slip difficult along this plane during (elastic) mechanical bending. (c), (d) Energy frameworks showing total intermolecular interaction energies. The thickness of tube represents the magnitude of energy (scale factor is 35, tube size 100 and energy cut-off is 5 kJ/mol). (e) m-stacking of molecules along crystal growth direction ($E_{total} = ~ - 46$ KJ/mol). (f) and (g) FESEM images of microcrystals of **1** in its straight and bent geometries.

suggests that the pop-ins in molecular crystals occur due to sudden movement of the tip due to abrupt yielding of the compressed molecular layers underneath the tip when the force exceeds their resistive force, leading to intermittent plastic deformation.^[13a,b]

The structure of **1** was determined from single-crystal X-ray diffraction technique to establish a structural basis for the exceptional mechanical flexibility. These needle-shaped crystals which grow along [100] axis with two pairs of side faces, (0-11)/(01-1) and (0-1-1)/(011), crystallize in the orthorhombic polar space group P2₁2₁2₁ (Figure 2a,b and Figure S4). There is one molecule in the asymmetric unit, with nearly flat molecular conformation (Figure 2a). The molecule has a large aromatic surface with two S and two N heteroatoms. In the crystal, the molecules stack along [100] axis or crystal length to form columns. Molecules in the adjacent stacked columns are tilted with respect to each other to form a herringbone structure. The columns with respect to each other are arranged such that the weak interaction planes of one-row overlap with molecules from below row, hence the structure is devoid of slip planes (see, Figure 2a,b). As quantitative information of the intermolecular interactions is crucial for understanding the mechanical flexibility of crystals, we calculated the pairwise interaction energies from the energy frameworks calculations using Crystal Explorer software (see Figure 2c,d). The thickness of the tubes connecting each pair of molecules is proportional to the total intermolecular

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Figure 3. (a)-(f) Confocal optical microscope images showing step-wise mechanical bending of a nearly straight crystal of length $L \approx 75.6 \mu m$ (a and g) into an arcshape (f and m). (h)-(r) FL images of straight and bent crystals of 1 transducing light when excited at different positions. The yellow dotted arrows indicate the direction of light propagation. (s)-(t) FL spectra of straight and bent crystals collected at the end of the crystals excited at different positions. (u) Table of input distance-dependent FL colours at outputs 1 and 2.

interaction energy of the corresponding pair. The calculations suggest that the most dominant interactions in the structure are from aromatic stacking ($E_{total} = -46$ KJ/mol). The other edge-to-face aromatic interactions, involving C–H····N (d/Å, θ '°: 2.74Å, 137.92°; 2.55Å, 143.80°), C–H··· π (2.84Å) and S···S, in other directions, are much weaker (significant E_{total} values are ~-16, -17 KJ/mol and rest are below 10 KJ/mol; see supporting information, Figure S2).

Recent reports by us and others suggest that the exceptional elastic flexibility in organic crystals originates from buffering regions in crystal structures, typically consisting of soft interactions that accommodate elastic strain energy.^[8] On the other hand, crystals that with facile slip planes allow permanent movement of molecules leading to plastic (permanent) deformation. When a crystal is bent elastically, the outer arc is under tensile stress while the inner arc is under compressive stress. Recently, Worthy et al. examined the mechanism of an elastically bendable crystal consisting herringbone structure where molecules stack along the needle direction (via π - π , Cu- π).^[8d] Using an elaborate synchrotron diffraction study, they established that the elastic bending occurs via rotation of molecules with respect to each other. This mechanism could be applied to our flexible crystal as it has similar herringbone structure with dominant π -stacking interactions in the needle direction. In a herringbone structure, the rotation of molecules towards planarity facilitates compression at the inner arc while rotation in the opposite direction facilitates elongation at the outer arc of the crystal (Figure 2b). [8d] These changes store elastic strain in the crystal. Upon release of external stress, the molecules rotate in the reverse direction and regain original structure (release the elastic strain).^[8d] Our crystal does not have any facile slip planes in the structure, which is consistent with its insignificant plastic deformation before fracture. The large dispersive π -stacking and weak intermolecular interactions among adjacent molecules in other directions have been found in most elastically bendable organic crystals. ^[1] Such interactions are proposed to act as structural buffers, ^[1a] thus accommodating elastic strain in flexible elastic crystals, as in our case.

As the macrocrystals are highly flexible, to demonstrate their bendability in the microscale regime, we intended to mechanically cut and alter the geometry of a straight microcrystal into an arcshape by applying force using AFM cantilever tip (Supporting videos S3 and S4). Field emission electron microscope (FESEM) images of a microcrystal of 1 obtained via slow evaporation technique in acetonitrile/methanol exhibited its smooth surface in straight and bent geometries (Figure 2f,g). A representative nearly straight crystal of length L~ 75.6 µm with a slight bent of 5.5 μ m at the right terminal was selected (Figure 3a) and tip force was applied to the right side of the crystal to displace the crystal terminal to a distance of 8.6 μ m (Figure 3b). Similarly, the left side of the crystal was displaced to about 12 μm to reduce the gap between the two crystal termini to 70.3 μ m (Figure 3c). Notably, the crystal was not held by any external microholders during mechanical operation with tip. Further, the crystal termini remained displaced without regaining to its original straight-shape even after retracting the cantilever from the crystal. The apparent plasticity by the microcrystal suggests that crystal-substrate adherence energy is more significant than shape-regaining energy. By displacing the right and left side of the crystal further, a nearly arc-shaped crystal geometry with the terminal-to-terminal distance of 67.14 µm was accomplished (Figure 3d-f). During the micromechanical operation, the crystals achieved a strain of ~ 2.8% (supporting information, Figure S3) without damage,

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demonstrating excellent flexibility. Crystal without external damage at high strains is essential in optical waveguides, as the presence of defects (tip-made or inherent) of sizes larger than the half of the optical wavelength facilitates unwanted optical loss via scattering.



Figure 4. (a)-(d). Confocal optical microscope images showing the micromanipulation of a crystal with AFM cantilever tip. A crystal of length $L \approx 206 \ \mu\text{m}$ (a) was first approached and pressed with a tip. (b) The tip was retracted, leaving the crystal bent at the contact point. (c) The same procedure was applied again to bend the crystal further. (d) Similarly, the other end of the crystal so pressed, resulting in an arc-shaped crystal. (e) A second arc-shaped crystal-2 was made and placed adjacent to the crystal-1 shown in (d). (f) Retraction of the tip after pressing of crystal-2 with a shortest end-to-end distance of 166 $\ \mu\text{m}$. (g) Radius (*R*) of curvature of two-coupled crystal waveguides. The yellow rectangle shows the widths of the waveguides at the junction. (i) A close-up view FESEM image of the junction shown in (h).

For optical waveguiding studies, a confocal microscopy setup in a transmission mode geometry was used (see Supporting information). We used the same single flexible microcrystal (L~75.6 µm) before (Fig. 3g-I) and after (Figure 3m-r) bending it. Excitation (bottom objective 60×) of the left terminal of the straight crystal with a 405 nm laser exhibited a bright blue FL at the site of excitation (Figure 3h). The corresponding FL spectrum (collected with a top 150× objective) showed spectral maxima at 496, 532 and a shoulder around 600 nm (Figure 3s). Unusually, at the crystal termini (output-1), a green FL was out coupled with the disappearance of 496 nm peak in the FL spectrum (Figure 3h,s). The outcoupled green light confirms that the crystal is acting as an active optical waveguide. The green light originates as a result of complete self-absorption of the light corresponding to $\lambda_{max} \approx 496$ nm peak (from 460 to 506 nm) during transduction of blue FL along the waveguide (Figure 3s and Figures S11 and S12).^[2e] The crystal was excited at a distance of 58.7, 40.4, 19.6, and 0 µm from the right terminal (Figure 3i-I). The corresponding spectra exhibited green, green, blue-green and blue FL at the right terminal (output-1) and blue-green, green, green, and green FL signals at the left terminal (output -2) (Figure 3u). The intensity of the 496 nm FL peak also increased while moving the excitation positions from 75.6 to 0 μ m due to decrease of the optical path length (Figure 3s). We have repeated the waveguiding studies with the bent crystal (Figure 3m-r). The FL images presented in Figure 3t demonstrate the outcoupling of light of different colour (as in a straight crystal) at both the termini of the crystal after propagating in the bent direction. Remarkably, the FL signal counts (15k) obtained at the output of flexible waveguide before and after bending were nearly the same (Figures 3s and t). The efficient transmission of optical signals of different colours by the flexible crystal waveguide demonstrates its use in flexible WDM technologies.

Earlier, the directional coupling behaviour was not observed in two X-crossed straight organic waveguides;^[14] however, channel add filters have been made successfully using a combination of curved and straight organic dye-based nanofibres.^[15] Therefore, we envisioned to join two arc-shaped optical waveguides by micromanipulation. It is expected that, in the resultant organic directional coupler with four termini, the curved junction will facilitate the transfer of light from one waveguide to another, which is analogous to evanescent field coupling [16] and subsequent light transfer between two optical fibres in the tapered region. We selected a representative crystal-1 of $L \approx 206 \ \mu m$ (Figure 4a). By pressing the crystal top and bottom termini with AFM tip an arc-shaped crystal with a terminalto-terminal gap of $C \approx 156 \ \mu m$ was produced (Figure 4b-d). Similarly, a bent crystal-2 with a terminal-to-terminal distance of (Chord) C ≈ 173 µm was created and positioned adjacent to arcshaped crystal-1 (Figure 4e) such that the mid-point of two arcs is touching each other to facilitate the light transfer. Further, finetuning of crystal-2 with the tip provided a terminal-to-terminal gap of $C \approx 166 \ \mu m$ (Figure 4f). The radius of curvature (R) of both crystal-1 and -2 in the two-coupled waveguide geometry is $R \approx$ 172.5 and 202.5 µm, respectively (Figure 4g). The FESEM image of the directional coupler exhibited width (W) of \approx 2.9 and 2.4 μ m for crystal-1 and -2, respectively at the coupling junction without any noticeable gap (Figure 4h and i). The geometry of this singlecrystalline 2×2 directional coupler (2-inputs and 2-outputs) is such that coupling of light at any one of four termini (crystal-1 or -2) will transduce FL light to two of its opposite termini of crystal-1 and -2, one via direct out-coupling and the other via the junction between both waveguides. The method presents one of the efficient ways to split optical signals in different intensities.

To investigate the directional coupling property of coupled crystalline waveguides, we excited one of the terminals (left) of crystal-1 (Figure 5a, see input-1), which transduced the blue FL signal towards coupling junction, wherein the FL signal (after reabsorbance) was efficiently split into two, and out coupled as green FL at termini-1a and -1b. Remarkably, no FL signal was detected at terminal 1c, which confirms the directional coupling in coupled crystal waveguides. The corresponding FL spectra recorded at input-1, primary output-1a and secondary output-1b showed a variation of the signal strengths and weak optical modes. Within a waveguide, the direct light transmission efficiency from input-1 to output-1a was about 11%. The splitting ratio that is the distribution of FL signal intensity among primary (1a) and secondary (1b) outputs was about 90/10. Similar optical excitation at the right terminal of waveguiding crystal-1 produced (Figure 5b, see input 2) two split FL signals which were out coupled at termini 2a and 2b with a splitting ratio of 72 and 28, respectively. At terminal 2c no signal was recorded, reaffirming the efficient directional coupling of the fabricated photonic circuit. The out coupled FL intensity at 2a was about 6%. The splitting ratio at the secondary outputs, 1b and 2b is related to the optical

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Figure 5. (a)-(d) From top: Cartoon representation of two coupled crystalline waveguides acting as a 2×2 directional coupler with two inputs and two outputs when excited at any one of the four termini, confocal optical microscope and FL images and FL spectra. The red crosses represent no signal at the corresponding output. The yellow colour arrows show the light transducing directions. The numbers in red colours show the optical path-dependent light splitting ratio of a directional coupler.

path length (L_{op}) of propagating light (Figure 4g), which is 66 µm for the former and 90 µm for the latter. An increase of optical path length decreases the split ratio due to increased optical loss in addition to coupling loss at the coupling junction. Excitation of one of the termini of crystal-2 either at input-3 or -4 also produced corresponding out coupled split signals at 3a/3b or 4a/4b, with split ratios of 85/15 and 90/10, respectively (Figure 5c,d). As observed earlier in Figure 5a and 5b, the variation of the secondary output intensities indicates different optical path lengths taken by the transmitted signals. Further, depending upon the light input terminal, the same output exhibited entirely different optical modes (though poorly resolved) in the FL spectra, which further confirms the optical coupling between the two crystal waveguides (Figure S13).

In conclusion, the presented one-dimensional macrocrystal (1) with a high aspect ratio, formed by dithieno[3,2-a:2',3'-c] phenazine has demonstrated elasticity in a three-point bending test. However, micro-crystals of 1 which are deposited at a glass surface behaved like plastic crystals while applying AFM cantilever tip pressure owing to strong adhesion force between the surface and crystal which overpowered the crystal shape regaining energy. The discriminatory self-absorbance of part of the FL from 460 to 506 nm by the flexible crystal waveguides can be used to switch output signal colours (from green to blue) for WDM technologies by varying the optical path lengths of the transducing light. The crystal waveguides deposited at the surface can be mechanically bent with different chord lengths using AFM cantilever tip for creating unique flexible WDMs. Similarly, intricate photonic device structures such as 2×2 directional couplers can be produced by utilising two flexible crystals for efficiently splitting the optical signals with different split ratios. The presented proof-of-principle experiments which combine state-of-the-art mechanical micromanipulation and photonic studies of flexible microcrystals will hitch and expand the research frontiers of two diverse disciplines, namely *crystal engineering*^[17] and *organic photonics*^[2-5].

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^{a) S. Saha, M. K. Mishra, C. M. Reddy, G. R. Desiraju, Acc. Chem. Res. 2018, 51, 2957–2967; b) S. Ghosh, M. K. Mishra, S. B. Kadambi, U. Ramamurty, G. R. Desiraju, Angew. Chem. Int. Ed. 2015, 54, 2674–2678; c) M. K. Panda, S. Ghosh, N. Yasuda, T. Moriwaki, G. D. Mukherjee, C. M. Reddy, P. Naumov, Nat. Chem. 2015, 7, 65–72; d) L. Pejov, M. K. Panda, T. Moriwaki, P. Naumov, J. Am. Chem. Soc. 2017, 139, 2318–2328; e) P. Commins, D. P. Karothu, P. Naumov, Angew. Chem. Int. Ed. 2019, 58, 2–11.}

^[2] a) Y. S. Zhao, Organic Nanophotonics: Fundamentals and Applications. Springer Berlin Heidelberg, 2014; b) R. Chandrasekar, Phys. Chem. Chem. Phys. 2014, 16, 7173-7183; c) N. Mitetelo, D. Venkatakrishnarao,

COMMUNICATION

J. Ravi, M. Popov, E. Mamonov, T. V. Murzina, R. Chandrasekar, *Adv. Opt. Mater.* **2019**, *7*, 1801775; d) P. Hui, R. Chandrasekar, *Adv. Mater.* **2013**, *25*, 2963-2967; e) N. Chandrasekhar, S. Basak, M. A. Mohiddon, R. Chandrasekar, *ACS Appl. Mater. Inter.* **2014**, *6*, 1488-1494; f) V. V. Pradeep, M. Annadhasan, R. Chandrasekar, *Chem. Asian. J.* **2019**, *14*, 4577-4581; g) Y. Zhang, Q. Liao, X. G. Wang, J. N. A. Yao, H. B. Fu, *Angew. Chem. Int. Ed.* **2017**, *56*, 3616–3620; h) M. P. Zhuo, J. J. Wu, X. D. Wang, Y. C. Tao, Y. Yuan, L. S. Liao, *Nat. Commun.* **2019**, *10*, 9; i) N. Chandrasekhar, *R. Reddy, M. D. Prasad, M. S. Rajadurai, R. Chandrasekar, Cryst. Eng. Commun.* **2014**, *16*, 4696-4700; j) D. Venkatakrishnarao, M. A. Mohiddon, N. Chandrasekhar, R. Chandrasekar, *Adv. Opt. Mater.* **2015**, *3*, 1035-1040.

- a) Y. C. Tao, X. D.Wang, L. S. Liao, J. Mater. Chem. C. 2019, 7, 3443-3446;
 b) D. Venkatakrishnarao, R. Chandrasekar, Adv. Opt. Mater. 2015, 4, 112-119;
 c) D. Venkatakrishnarao, E. V. Mamonov, T. V. Murzina, R. Chandrasekar, Adv. Opt. Mater. 2018, 6, 1800343;
 d) K. Tabata, D. Braam, S. Kushida, L. Tong, J. Kuwabara, T. Kanbara, A. Beckel, A. Lorke, Y. Yamamoto, Sci. Rep. 2014, 4, 5902;
 e) J. Ravi, D. Venkatakrishnarao, C. Sahoo, S. R. G. Naraharisetty, N. Mitetelo, A. A. Ezhov, E. Mamonov, T. Murzina, R. Chandrasekar, Chem. Nano. Mat, 2018, 4, 764;
 f) D. Venkatakrishnarao, C. Sahoo, S. A. Mamonov, I. A. Kolmychek, A. I. Maydykovskiy, N. V. Mitetelo, V. B. Novikov, S. R. G. Naraharisetty, T. V. Murzina, R. Chandrasekar, J. Mater. Chem. C 2017, 5, 12349-12353;
 g) V. V. Pradeep, N. Mitetelo, M. Annadhasan, E. Mamonov, T. V. Murzina, R. Chandrasekar, Adv. Opt. Mater. 2020, 8, 1901317.
- [4] a) W. Zhang, J. Yao, Y. S. Zhao, *Acc. Chem. Res.* 2016, *49*, 1691-1700;
 b) X. Wang, Q. Liao, H. Li, S. Bai, Y. Wau, X. Lu, H. Hu, Q. Shi, H. Fu, *J. Am. Chem. Soc.* 2015, *137*, 9289-9295; c) X. Wang, Q. Liao, Q. Kong, Y. Zhang, Z. Xu, X. Lu, H. Fu, *Angew. Chem.* 2014, *126*, 5973-5977; d)
 D. Venkatakrishnarao, Y. S. L. V. Narayana, M. A. Mohaiddon, E. A. Mamonov, I. A. Kolmychek, A. I. Maydykovskiy, V. B. Novikov, T. V. Murzina, R. Chandrasekar, *Adv. Mater.* 2017, *29*, 1605260.
- [5] a) K. Takazawa, J. Inoue, K. Mitsuishi, T. Kuroda, T. Adv. Funct. Mater. 2013, 23, 839-845; b) K. Takazawa, J.-I. Inoue, K. Mitsuishi, T. Takamasu, Adv. Mater. 2011, 23, 3659; c) C. Zhang, C.-L. Zou, Y. Zhao, C.-H. Dong, C. Wei, H. Wang, Y. Liu, G.-C. Guo, J. Yao, Y. S. Zhao, Sci. Adv., 2015, 1, e1500257.
- [6] a) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Bredas, *Chem. Rev*, 2007, 107, 926–952; b) A. N. Lakshminarayana, A. Ong, C. Chi, *J. Mater. Chem.* C, 2018, 6, 3551-3563; c) J. Dhar, U. Salzner, S. Patil, *J. Mater. Chem.* C, 2017, 5, 7404 —7430; d) K. -J. Baeg, M. Caironi, Y.-Y. Noh, *Adv. Mater.*, 2013, 25, 4210 —4244; e) A. Asatkar, S. P. Senanayak, A. Bedi, S. Panda, K. S. Narayan, S. S. Zade, *Chem. Comm.* 2014, *50*, 7036-7039; g) A. Z. Ashar, K. S. Narayan, *Org. Electron.* 2017, *42*, 8-12; h) D. Kim, M. R. Reddy, K. Cho, D. Ho, C. Kim, S.-Y. Seo, *Org. Electron.* 2020, *76*, 105464.
- [7] X. Guo, Y. Xu, S. Ogier, T. N. Ng, M. Caironi, A. Perinot, L. Li, J. Zhao, W. Tang, R. A. Sporea, A. Nejim, J. Carrabine, P. Cain, F. Yan, *IEEE Trans. Electron Devices*, **2017**, *64*, 1906 -1921.
- [8] a) S. Ghosh, C. M. Reddy, Angew. Chem., Int. Ed. 2012, 51, 10319-10323; b) S. Dey, S. Das, S. Bhunia, R. Chowdhury, A. Mondal, B. Bhattacharya, R. Devarapalli, N. Yasuda, T. Moriwaki, K. Mandal, G. D. Mukherjee, C. M. Reddy, Nat. Commun. 2019, 10, 3711; c) M. Đaković, M. Borovina, M. Pisačić, C. B. Aakeröy, Ž. Soldin, B. M. Kukovec, I.

Kodrin, *Angew. Chem. Int. Ed.* **2018**, *57*, 14801–14805; d) A. Worthy, A. Grosjean, M. C. Pfrunder, Y. Xu, C. Yan, G. Edwards, J. K. Clegg, J. C. McMurtrie, *Nat. Chem.* **2018**, *10*, 65–69.

- [9] a) S. Hayashi, T. Koizumi, Angew. Chem. Int. Ed. 2016, 55, 2701-2704;
 b) H. Liu, Z. Lu, Z. Zhang, Y. Wang, H. Zhang, Angew. Chem. Int. Ed. 2018, 57, 8448-8452;
 c) R. Huang, C. Wang, Y. Wang, H. Zhang, Adv. Mater. 2018, 30, 1800814;
 d) 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;
 e) J. M. Halabi, E. Ahmed, L. Catalano, D. P. Karothu, S. C. 2019, 141, 14966-14970.
- [10] a) S. Saha, G. R. Desiraju, J. Am. Chem. Soc. 2017, 139, 1975-1983; b)
 G. R. Krishna, R. Devarapalli, G. Lal, C. M. Reddy, J. Am. Chem. Soc. 2016, 138, 13561–13567; c) G. R. Krishna, M. S. R. N. Kiran, C. L. Fraser, U. Ramamurty, C. M. Reddy, Adv. Funct. Mater. 2013, 23, 1422 1430; d)
 J. Harada, T. Shimojo, H. Oyamaguchi, H. Hasegawa, Y. Takahashi, K. Satomi, Y. Suzuki, J. Kawamata, T. Inabe, Nat. Chem. 2016, 8, 946-952; d)
 S. Takamizawa, Y. Takasaki, T. Sasaki, N. Ozaki, Nat. Commun. 2018, 9, 3984; e)
 B. Kahr, M. D. Ward, Nat. Chem. 2018, 10, 4-6; f) L. O. Alimi, P. Lama, V. J. Smith, L. J. Barbour, Chem. Commun. 2018, 54, 2994-2997; g)
 S. Hu, M. K. Mishra, C. C. Sun, Chem. Mater. 2019, 31, 3818-3822; h)
 T. Seki, C. Feng, K. Kashiyama, S. Sakamoto, Y. Takasaki, T. Sasaki, S. Takamizawa, H. Ito, Angew. Chem., Int. Ed. 2020, DOI: 10.1002/anie.201914610; i)
 A. Mondal, B. Bhattacharya, S. Das, S. Bhunia, R. Chowdhury, S. Dey, C. M. Reddy, Angew. Chem. Int. Ed. 2020, 132, 2-12.
- a) S. Basak, R. Chandrasekar, J. Mater. Chem. C, 2014, 2, 1404–1408;
 b) M. Annadhasan, D. P. Karothu, R. Chinnasamy, L.Catalano, E. Ahmed, S. Ghosh, P. Naumov, R. Chandrasekar, Angew. Chem. Int. Ed. 2020, 10.1002/anie.202002627.
- [12] S. Somekh, Optical Directional Couplers. In: Barnoski M.K. (eds) Introduction to Integrated Optics, 1974, Springer, Boston, MA.
- [13] a) S. Varughese, M. Kiran, U. Ramamurty, G. R. Desiraju, Angew. Chem. Int. Ed. 2013, 52, 2701-2712; b) M. S. R. N. Kiran, S. Varughese, C. M. Reddy, U. Ramamurty, G. R. Desiraju, Cryst. Growth Des. 2010, 10, 4650-4655; c) W.C. Oliver, G. M. Pharr, J. Mater. Res. 2004, 19, 3– 20; d) R. Devarapalli, S. B. Kadambi, C. T. Chen, G. R. Krishna, B. R. Kammari, M. J. Buehler, U. Ramamurty, C. M. Reddy, Chem. Mater. 2019, 31, 1391–1402.
- a) Y. S. Zhao, J. Xu, A. Peng, H. Fu, Y. Ma, L. Jiang, J. Yao, Angew. Chem. Int. Ed. 2008, 47, 7301-7305; b) W. Guo, H. Ding, P. Zhou, Y. Wang, B. Su, Angew. Chem. Int. Ed. 2020, 59, 6745-6749; c) N. Chandrasekhar, M. A. Mohiddon, R. Chandrasekar, Adv. Opt. Mater. 2013, 1, 305-311.
- [15] K. Takazawa, J.-I. Inoue, K. Mitsuishi, ACS Appl. Mater. Interfaces 2013, 5, 6182-6188.
- [16] W. Talataisong, R. Ismaeel, G. Brambilla, Sensors, 2018, 18, 461.
- [17] a) G. R. Desiraju, J. J. Vittal, A. Ramanan, Crystal Engineering: A Textbook, World Scientific, 2011; b) G. R. Desiraju, Crystal Engineering. The Design of Organic Solids, Elsevier, Amsterdam, 1989; c) C. M. Reddy in Engineering Crystallography: From Molecule to Crystal to Functional Form (Eds.: K. J. Roberts, R. Docherty, R. Tamura), Springer, Dordrecht, 2017, pp. 425–435.

COMMUNICATION

Entry for the Table of Contents



Flexible microcrystals of dithieno[3,2-a:2',3'-c]phenazine exhibit excellent optical waveguiding and wavelength division multiplexing properties in both straight and bent geometries during mechanical micromanipulation with AFM cantilever tip. Phenomenally, a futuristic 2×2 directional coupler made from two bent crystals via micromanipulation split the optical signal in two different split ratios depending upon the optical propagation path length.