Supporting information

Decimeter-Length Elastic Organic Crystals Capable of Mechanical Post-Processing and Optical Waveguide Modulating at 77 K

General information

All chemicals for syntheses were purchased from commercial sources. The solvents for syntheses were analytical-reagent grade and were used without further purification. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 MHz and 500 MHz spectrometer with tetramethylsilane as an internal standard, respectively. The mass spectrum was recorded on a Bruker micrOTOF QII mass spectrometer. The UV-vis absorption spectra were recorded with a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded with a Shimadzu RF-5301PC spectrometer or an Ocean Insight Maya2000 Pro spectrometer. The mechanical tests were carried out on no. 5944 Universal Testing System from Instron. The fluorescence quantum yields were determined by using a Hamamatsu Quantaurus-QY spectrometer. The fluorescence lifetime was measured on Edinburgh FLS920 using a time-correlated single-photon (TCSPC) module.

Single crystal X-ray measurements: Single crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer with Mo radiation. The structures were solved with direct methods using the Olex2 programs and refined with full-matrix least-squares on F². Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically.

Optical waveguiding tests: The crystal was irradiated by the third harmonic (355 nm) of a Nd:YAG (yttrium-aluminum-garnet) laser at a repetition rate of 10 Hz and a pulse duration of about 10 ns. The energy of the laser was adjusted by using the calibrated neutral density filters. The beam was focused into a dot by using a condensing lens. The emission was detected at one end of the crystal using a Maya2000 Pro CCD spectrometer. The optical loss coefficients (α) were obtained by a single exponential fitting of the function $I_{tip} / I_{body} = A \exp(-\alpha D)$, where I_{tip} and I_{body} were the fluorescence intensities of out-coupled and incidence light, and D was the distance between the excited site and the tip where the emission was collected.



Figure S1. Synthetic route for compound 1.

Tetrafluoroterephthalonitrile (2.01 g, 10 mmol) was dissolved in 50 mL of tetrahydrofuran, then 2-(2-aminoethoxy)-1-ethanol (1.05 g, 10 mmol) and 4 mL of triethylamine solution were added and stirred at room temperature. The reaction was monitored by thin layer chromatography and after about 8 h the tetrahydrofuran was evaporated on a rotary evaporator. The reaction mixture was dissolved in dichloromethane, washed several times with saturated brine, the organic phase dried over anhydrous sodium sulphate and concentrated under vacuum. The crude compound was purified by column chromatography using ethyl acetate and dichloromethane (1:5) as eluent to give a pale-yellow product in 75% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 7.00 (s, 1H), 4.58 (t, J = 5.1 Hz, 1H), 3.63 (dt, J = 15.8, 5.4 Hz, 4H), 3.44 (dq, J = 8.5, 4.6 Hz, 4H). ¹³C NMR (101 MHz, DMSO-d₆) δ 149.74, 148.79, 147.21, 146.46, 139.24, 138.38, 138.24, 136.94, 112.35, 109.02, 97.19, 89.87, 72.73, 69.79, 60.67, 44.22. MS (m/z): 286.07 [M⁺] (calcd: 285.07).



Figure S2. Synthetic route for compound 2.

Tetrafluoroterephthalonitrile (2.0152 g, 10 mmol) was dissolved in 40 mL of tetrahydrofuran. Subsequently, triethylamine (4 mL, 40 mmol) was added, and the mixture was stirred at room temperature. Propanolamine (0.7512 g, 10 mmol) was dissolved in 10 mL of tetrahydrofuran and added dropwise to the reaction mixture via a constant-pressure dropping funnel. Reaction progress was monitored by thin-layer chromatography, and the feedstock was fully consumed within approximately 9 hours. The tetrahydrofuran was evaporated on a rotary evaporator. The resulting reaction mixture was dissolved in dichloromethane, subjected to multiple washes with saturated saline, and the combined organic extracts were desiccated over sodium sulfate. Subsequent concentration under vacuum ensued. The compound underwent purification via column chromatography using an eluent composed of ethyl acetate and dichloromethane in a 1:5 ratio. The yield of compound 2 was 65%. ¹H NMR (400 MHz, DMSO-d₆) δ 7.13 (s, 1H), 4.61 (t, *J* = 4.8 Hz, 1H), 3.57 (q, *J* = 6.8 Hz, 2H), 3.49 (q, *J* = 5.8 Hz, 2H), 1.75 (p, *J* = 6.7 Hz, 2H). MS (m/z): 256.10 [M⁺] (calcd: 255.06).



^{f1} (ppm) **Figure S4.** ¹³C NMR spectrum of compound **1** (101 MHz, DMSO-d₆).

Figure S5. ¹H NMR spectrum of compound 2 (400 MHz, DMSO-d₆).

Figure S6. Photograph of a decimeter-length crystal 1.

Figure S7. Decay curves of crystals 1 (a) and 2 (b).

Figure S8. Photographs of crystals 1 (a) and 2 (b) repeatedly bent at 77 K.

Figure S9. Face indexing of crystals 1 (a) and 2 (b) with typical habit.

Figure S10. Energy frameworks viewed along the c-axis for crystals 1 (a) and 2 (b).

Figure S11. Photograph of fluorescence of crystal 1 after machining.

Figure S12. Emission spectra collected at a straight crystal tip of different widths: 0.372 mm (a), 0.300 mm (b), 0.228 mm (c) and 0.072 mm (d).

Figure S13. The I_{tip} / I_{body} decays of different widths: 0.372 mm (a), 0.300 mm (b), 0.228 mm (c) and 0.072 mm (d).

Figure S14. Normalized fluorescence spectra of acquisitions at different excitation positions of different widths: 0.372 mm (a), 0.300 mm (b), 0.228 mm (c) and 0.072 mm (d).

Figure S15. Relationship between width and wavelength variation of crystal 1.

Figure S16. Emission spectra collected at a bent crystal tip of different widths at 298 K, 0.372 mm (a) and 0.072 mm (c). The I_{tip} / I_{body} decays of different widths at 298 K, 0.372 mm (b) and 0.072 mm (d).

Figure S17. Emission spectra collected at a bent crystal tip of different widths at 77 K, 0.372 mm (a) and 0.072 mm (c). The I_{tip} / I_{body} decays of different widths at 77 K, 0.372 mm (b) and 0.072 mm (d).

		ε / %	e / %	<i>t /</i> mm	d / mm	e / %	<i>t</i> / mm	d/mm	e / %
t / mm (1)	<i>d /</i> mm (1)	(1)	(1)	(2)	(2)	(2)	(2)	(2)	(2)
		(1) (298 K)	(77 K)	(298 K)	(298 K)	(298 K)	(77 K)	(77 K)	(77 K)
0.014	0.52	2.62	2.62	0.017	0.58	2.85	0.068	13.195	0.51
0.023	0.52	4.24	4.24	0.020	0.58	3.33	0.068	10.227	0.66
0.028	0.52	5.11	5.11	0.025	0.58	4.13	0.076	11.05	0.68
0.029	0.52	5.28	5.28	0.031	0.58	5.07	0.034	4.918	0.69
0.034	0.52	6.14	6.14	0.031	0.58	5.07	0.031	4.427	0.70
0.037	0.52	6.64	6.64	0.031	0.58	5.07	0.054	6.905	0.78
0.039	0.52	6.98	6.98	0.031	0.58	5.07	0.059	7.264	0.81
0.040	0.52	7.14	7.14	0.036	0.58	5.84	0.028	3.382	0.82
0.041	0.52	7.31	7.31	0.036	0.58	5.84	0.031	3.655	0.84
0.042	0.52	7.47	7.47	0.036	0.58	5.84	0.067	7.464	0.89
0.042	0.52	7.47	7.47	0.046	0.58	7.35	0.052	5.686	0.91
0.043	0.52	7.64	7.64	0.050	0.58	7.94	0.048	4.927	0.96
0.045	0.52	7.96	7.96	0.052	0.58	8.23	0.141	14.295	0.98
0.048	0.52	8.45	8.45	0.053	0.58	8.37	0.034	3.223	1.04
0.055	0.52	9.57	9.57	0.058	0.58	9.09	0.099	8.681	1.13
ε / %		6.98	7.47	ε/	%	8.23	3	/ %	0.83

Table S1 Relationship between crystal thickness and the maximum elastic strain $\varepsilon = (t / (t + d))$. Red indicates cracked crystals.

Table S2 Hydrogen bonding energies of crystal 1 at 298 K and 100 K.

H-bonds (1)	bond energy (298 K)	bond energy (100 K)
(a) C−H····N	-0.515 kcal mol ⁻¹	-1.740 kcal mol ⁻¹
(b) C−H····F	-0.158 kcal mol ⁻¹	-0.739 kcal mol ⁻¹
(c) C–H····N	-0.624 kcal mol ⁻¹	-1.632 kcal mol ⁻¹
$(\mathbf{d}) \operatorname{C-H} \cdots \operatorname{F}$	-0.175 kcal mol ⁻¹	-0.697 kcal mol ⁻¹
(e) O−H····O	-3.744 kcal mol ⁻¹	-4.658 kcal mol ⁻¹
(f) O−H···O	-5.758 kcal mol ⁻¹	-4.674 kcal mol ⁻¹
(g) N−H····O	-3.663 kcal mol ⁻¹	$-4.259 \text{ kcal mol}^{-1}$

H-bonds (2)	bond energy (298 K)	bond energy (100 K)
(a) C−H····N	-4.692 kcal mol ⁻¹	-2.146 kcal mol ⁻¹
(b) N−H···O	-6.261 kcal mol ⁻¹	-5.558 kcal mol ⁻¹
(c) C–H···F	-6.080 kcal mol ⁻¹	-5.481 kcal mol ⁻¹
$(\mathbf{d}) \operatorname{C-H} \cdots \operatorname{F}$	-1.019 kcal mol ⁻¹	-0.828 kcal mol ⁻¹

Table S3 Hydrogen bonding energies of crystal **2** at 298 K and 100 K.

Table S4 Crystallographic data of crystals 1 and 2 at 298 K and 100 K.

Empirical formula	$C_{12}H_{10}F_3N_3O_2$	$C_{12}H_{10}F_3N_3O_2$	C ₁₁ H ₈ F ₃ N ₃ O	C ₁₁ H ₈ F ₃ N ₃ O	
Formula weight	285.23	285.23	255.20	255.20	
Temperature / K	298.0	100.0	298.0	100.0	
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	
Space group	P na 2_1	Pna2 ₁	<i>P</i> 2 ₁ / n	<i>P</i> 2 ₁ / n	
<i>a</i> / Å	13.4921(4)	13.3841(8)	9.7492(8)	9.6318(4)	
<i>b</i> / Å	17.9826(6)	17.8129(10)	6.1659(5)	6.3855(2)	
<i>c</i> / Å	5.1708(10)	5.0896(2)	18.7972(16)	17.9069(8)	
α/°	90	90	90	90	
β/°	90	90	91.957(3)	93.530(2)	
γ / °	90	90	90	90	
Volume / Å ³	1254.56(6)	1213.41(11)	1129.29(16)	1099.25(7)	
Z	4	4	4	4	
Density / g cm ⁻³	1.510	1.561	1.501	1.542	
μ / mm ⁻¹	0.135	0.139	0.134	0.137	
F (000)	584.0	584.0	520.0	520.0	
Goodness-of-fit on F ²	1.060	1.049	1.060	1.033	
R_1	0.0455	0.0310	0.0534	0.0311	
wR_2	0.0882	0.0790	0.0828	0.0788	
CCDC No.	2380818	2380823	2380824	2380828	

Legends for the supplementary movie

Supplementary Movie 1. Room temperature crystal machining.
Supplementary Movie 2. LN temperature processing of PDMS.
Supplementary Movie 3. LN temperature processing of crystal.
Supplementary Movie 4. Real-Time 2D motion monitoring in cryogenic environments.