Curving deformation-induced photoluminescence changes and anisotropy analysis in elastic organic crystals

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Experiential

UV-vis absorption spectra were obtained on an Ocean Optics USB4000-XR1 fiber spectrometer with a DH2000-BAL tungsten halogen light source. PL spectra were obtained on an Ocean Optics USB4000 fiber spectrometer with a LSM LED light source. PL spectrum was measured on a JASCO model FP-8500 spectrophotometer. Spatially resolved μPL spectra were measured by an analyzing system (405 nm UV laser OptoSigma LDU33-405-3.5, micro-PL spectra using a USB400 and a R200-7-UV-VIS probe) recorded by a CCD (detector: Sony ILX511B linear silicon CCD array). The excitation laser was filtered with a band-pass filter (YIF-BA460IFS) and focused on the microrod with an objective (5×, NA = 0.15). The collected emission was then guided to a spectrometer (Lambda Vision SA-100A) and recorded by a CCD (detector: Hamamatsu photonics S11151-2048 CCD linear image sensor). PL anisotropy was measured by the excitation of polarized 405 nm UV laser. The single crystal X-ray diffraction data for single crystals were collected at room temperature using a SMART APEX II (Bruker AXS) diffractometer with a CCD detector. The crystal structures were solved by the direct method and refined by full matrix least-squares using SHELXTL. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method using SHELXL-2014. Hydrogen atoms were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. Powder XRD patterns of straight and bent crystals were collected with Bruker Advance diffractometer: Cu K_α radiation, voltage = 40 kV, and current = 40 mA. Data were collected at $2\theta = 5$ to 25° at a continuous scan rate of 1.0°/min.

Calculation

DFT calculation was performed using Gaussian 03 suit of programs by optimization with using the B3LYP/6-31G(d,p) method. The orbital diagrams were generated by using the GaussView program.

Hirshfeld surface and energy frameworks were calculated by CrystalExplorer.

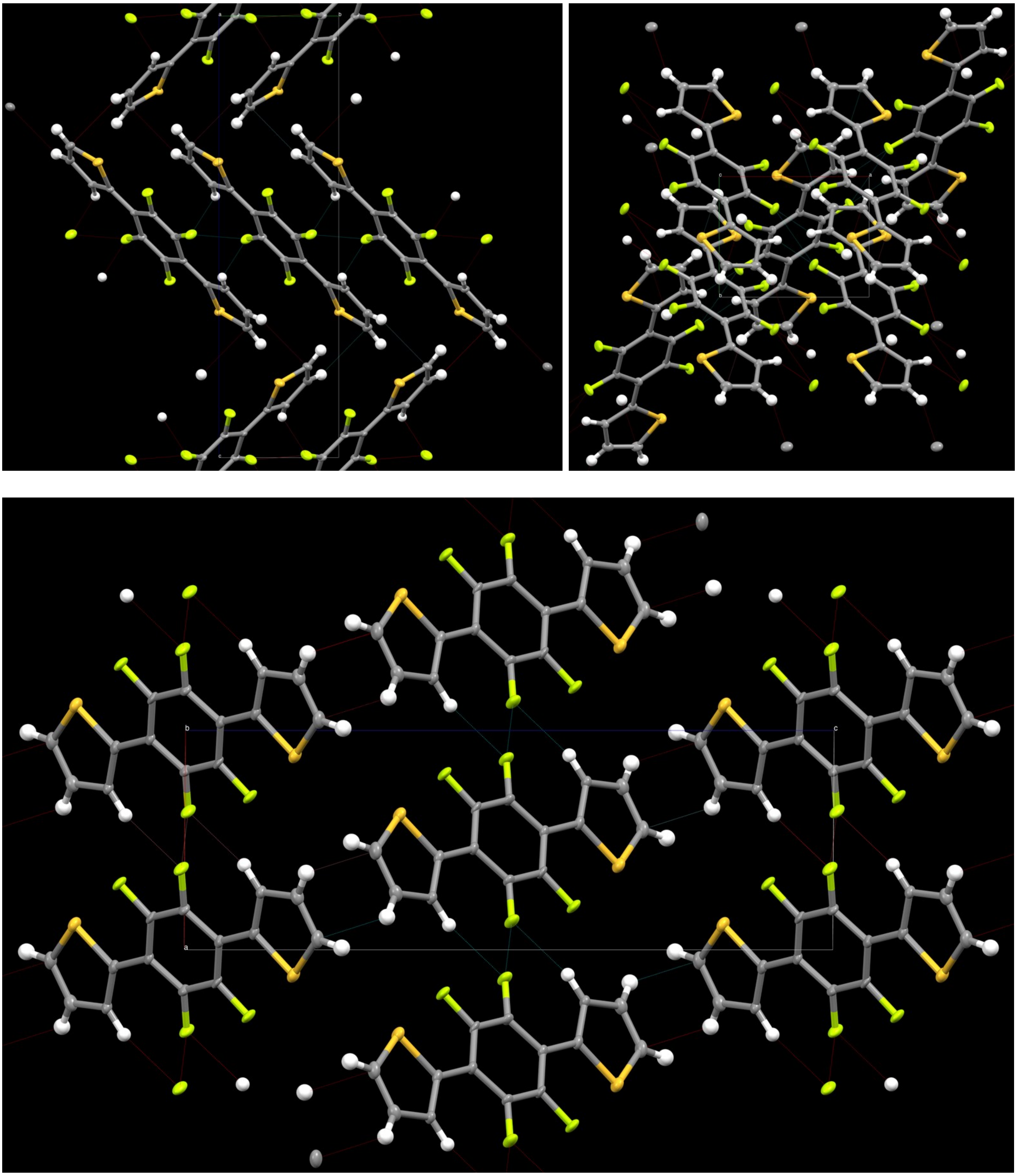


Fig. S1 Crystal structure. Green and red lines are F---F and H---F contacts.

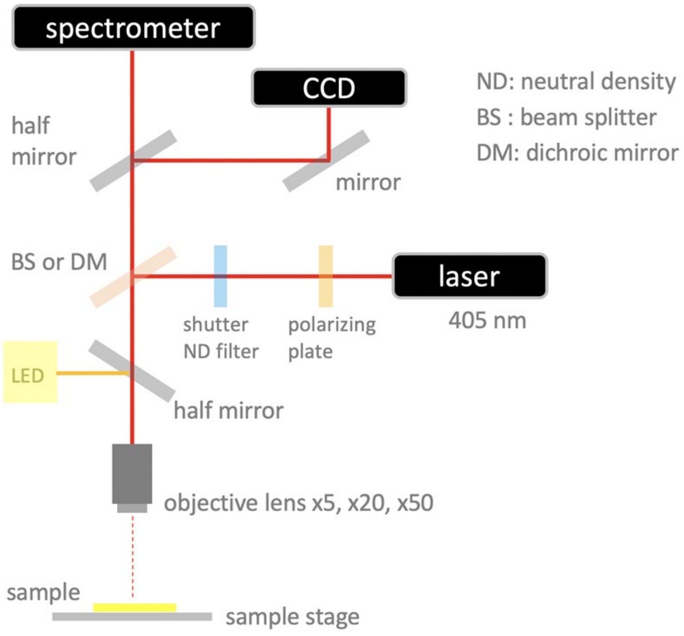


Fig. S2 Schematic illustration of spatially resolved μPL measurement.

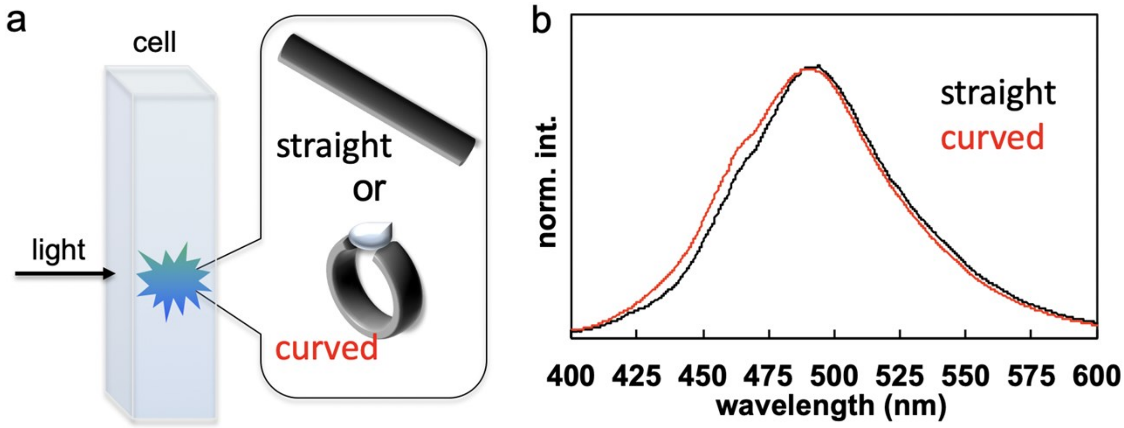


Fig. S3 (a) Measurement of straight and curved crystals. (b) PL spectra of straight and curved crystals.

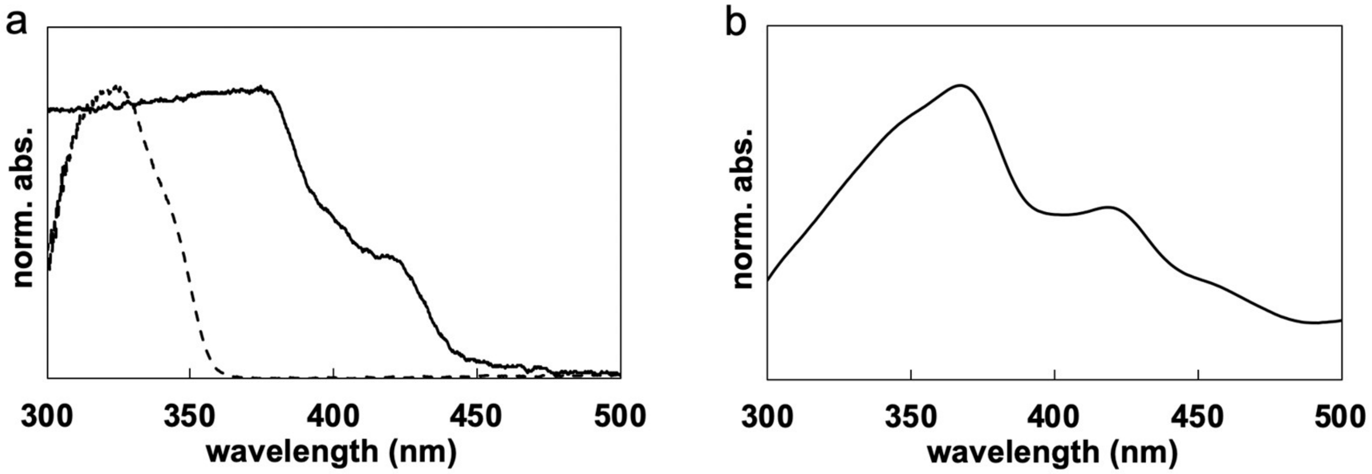


Fig. S4 (a) UV-vis absorption spectra in a dichloromethane solution (dotted line) and crystal (solid line). (b) Excitation spectrum in crystal. Exc. WL: 500 nm.

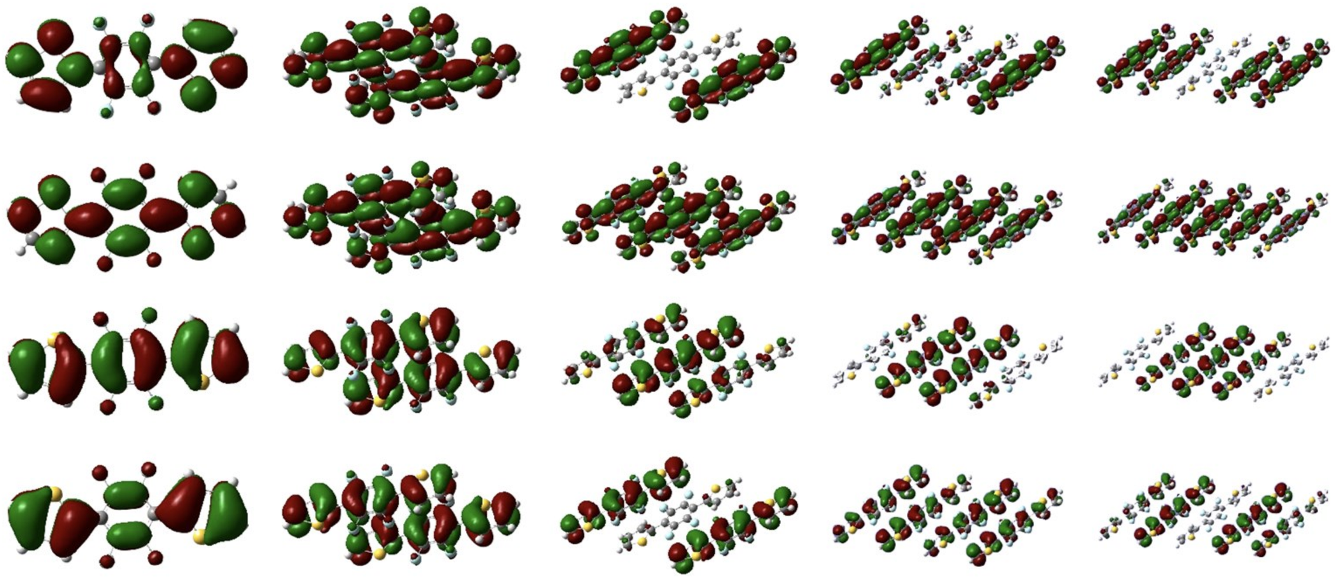


Fig. S5 Electron cloud distribution of the HOMO-1, HOMO, LUMO, and LUMO+1, Isovalue: 0.02.

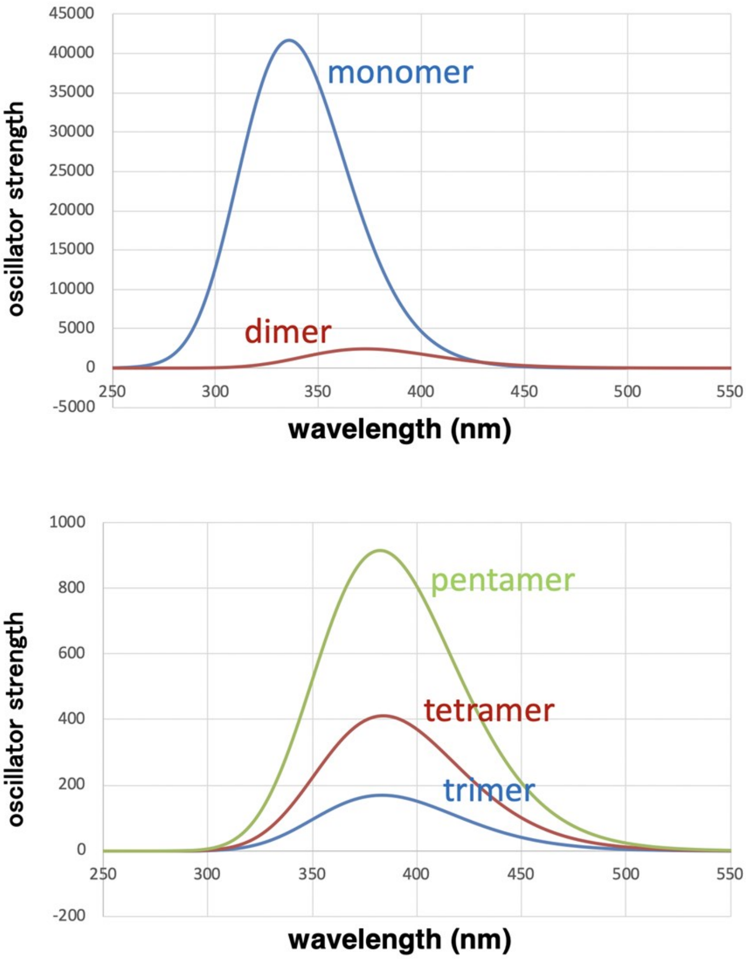


Fig. S6 Simulated electronic spectra of molecules in crystal.

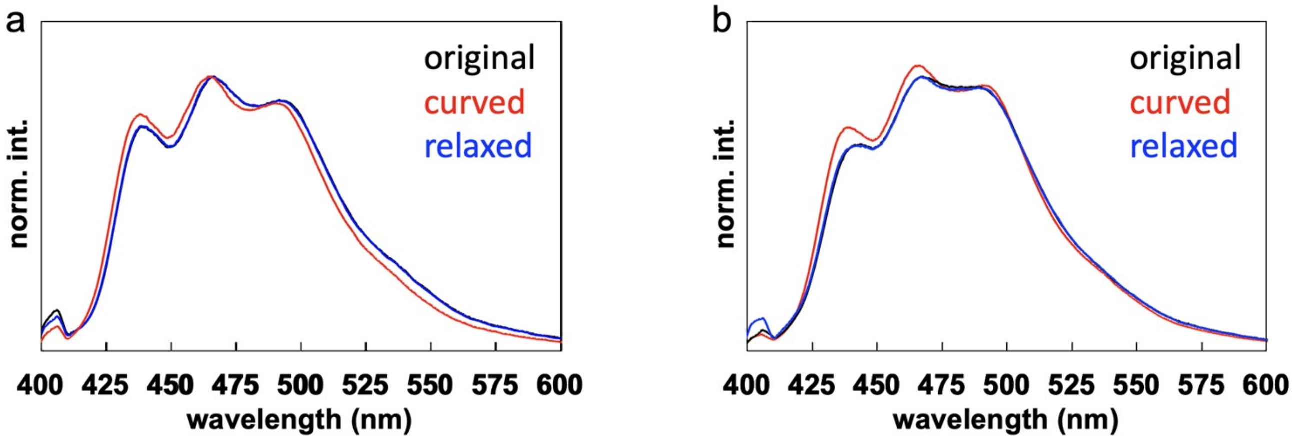


Fig. S7 (a) Spatially resolved μ-PL spectra of the curved crystal for (010) face measured at the outer crystal surface. (b) Spatially resolved μ-PL spectra of the curved crystal for (001) face measured at the outer crystal surface.

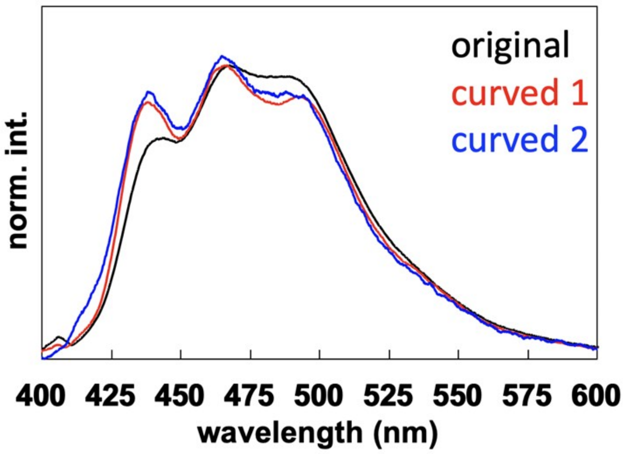


Fig. S8 (a) Spatially resolved μ-PL spectra of the curved crystal for (001) face measured at the outer crystal surface. Curved 1: ε= 2. Curved 1: ε= 2.5.

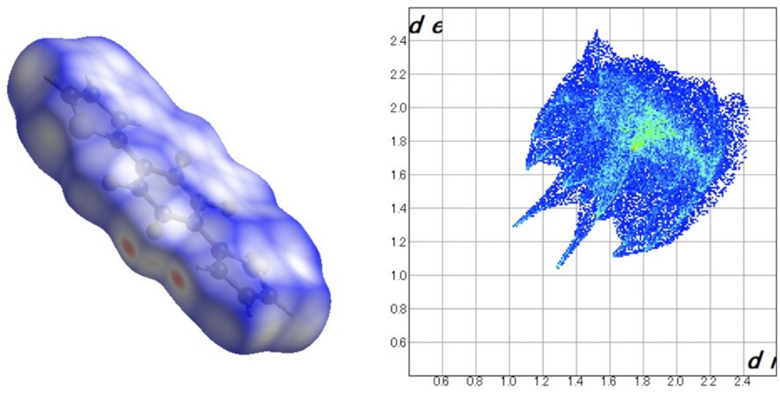


Fig. S9 Hirshfeld surface and the fingerprint plot of the crystal.

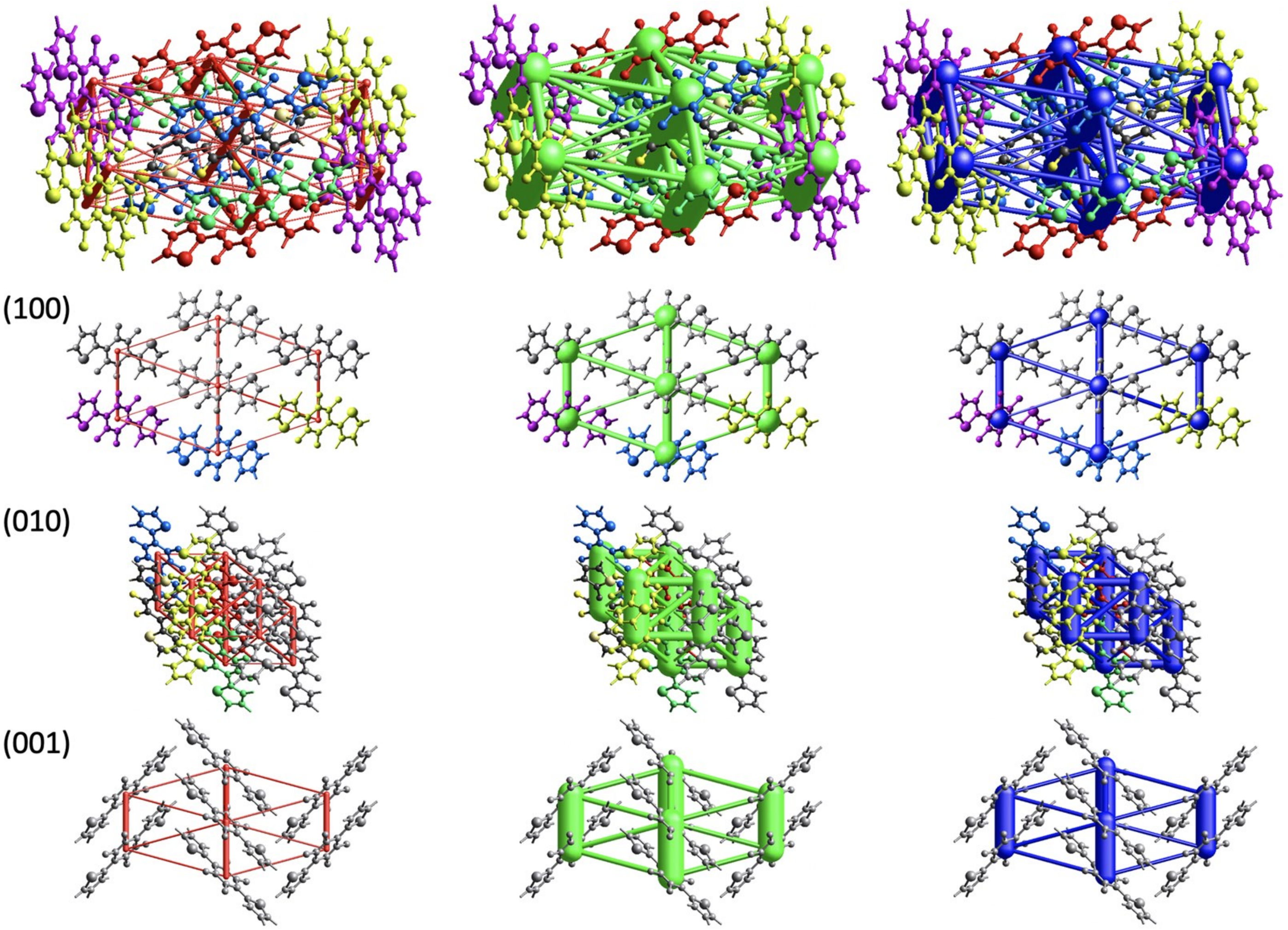


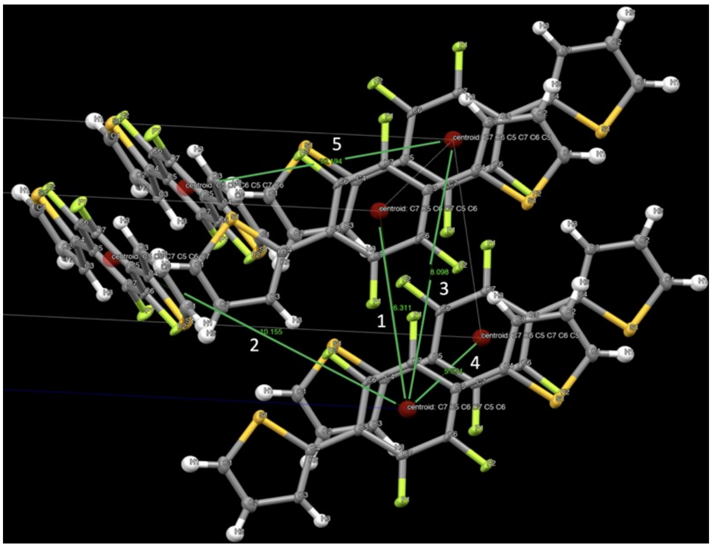
Fig. S10 The visualization of the interaction energies as the thickness of the cylinders connecting the centers of the molecules. Red frameworks: electrostatic total interaction energy. Green frameworks: dispersion total interaction energy. Blue frameworks: sum of total interaction energy.

Table S1 Stabilization energies (in kJ mol^{-1}) of the individual molecular pairs associated with different intermolecular interactions

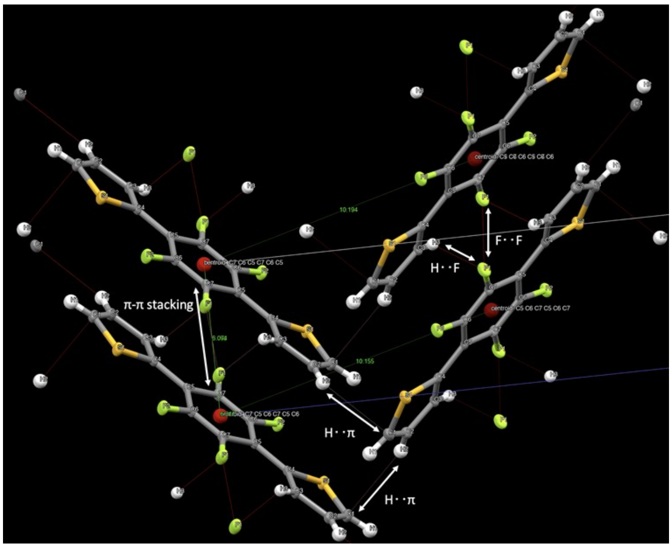
Motifs[a]	Symmetry operation	R[b], Å	E_{Coul}	E_{Pol}	E_{Disp}	E_{Rep}	E_{Tot}[c]	Contributed Interactions[d]
1	x, y, z	6.31	-2.4	-0.5	-24.8	8.2	-19.4	F…F, H…F
2	-x+1/2, y+1/2, -z+1/2	10.16	-2.2	-0.4	-7.0	5.8	-5.1	H…π
3	x, y, z	8.10	-6.4	-0.7	-18.1	14.6	-14.1	F…F, H…F
4	x, y, z	5.07	-13.5	-1.0	-70.1	45.9	-47.8	π-π stacking
5	-x+1/2, y+1/2, -z+1/2	10.19	-3.9	-0.6	-14.4	12.5	-9.4	H…π

[a] Type of motifs is below ***a***. [b] The distance between molecular centroids (mean atomic position). [c] Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately. [d] Interactions are shown in below ***b***.

a.



b.



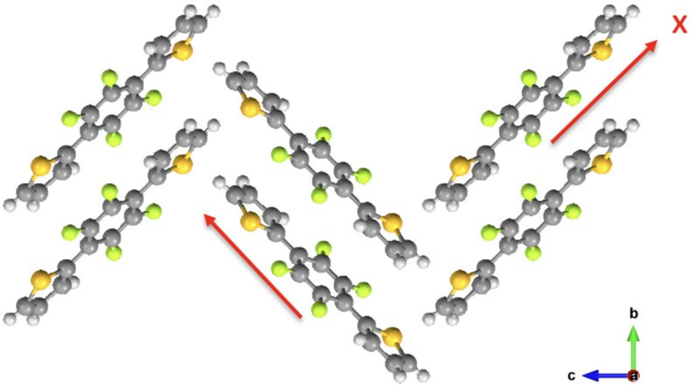


Fig. S11 Transition dipole moment in crystal.

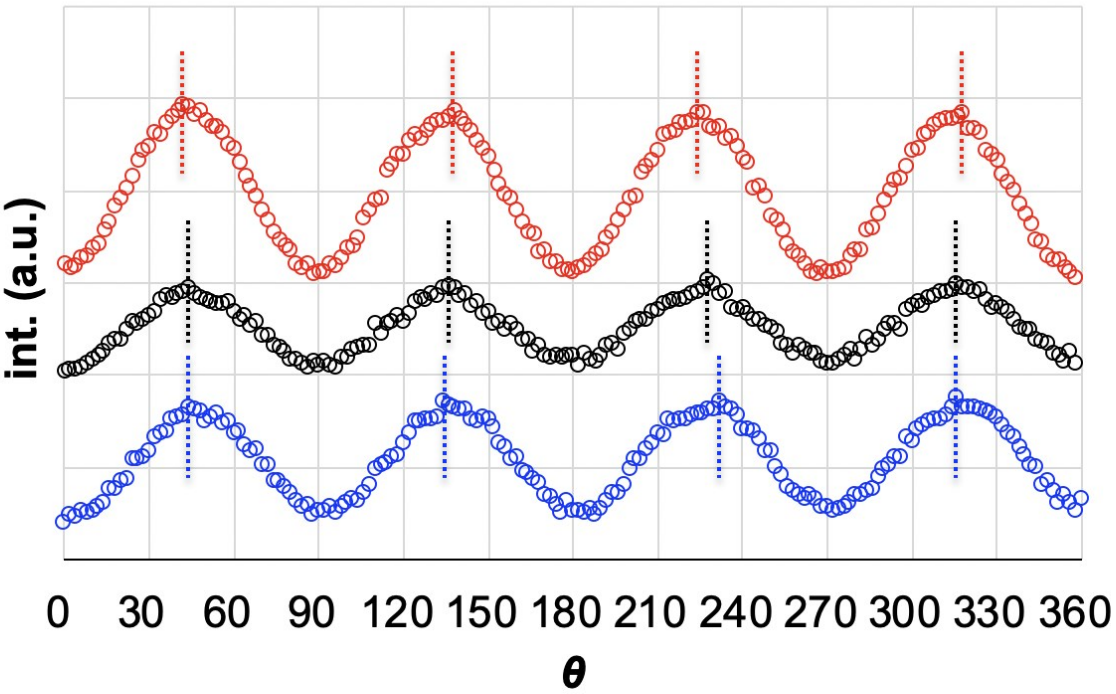


Fig. S12 Incident polarization angle-dependent PL intensities for (001) face of the curved crystal. Monitored wavelength: 500 nm. Red: outside. Black: center. Blue: inside.