SUPPORTING INFORMATION

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Flexible Organic Single Crystal with Elastic Bending and Plastic Twisting Capabilities

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n EXPERIMENTAL

1,2-Bis(3-bromophenyl)ethane-1,2-dione (**BBPED**) was supplied by Bide Pharmatech Ltd and purified by column chromatography before use. All solvents were purchased from Beijing Chemical Works. 1H NMR (600 MHz) spectra were recorded on a Mercury Plus instrument. The absorption/emission measurements were performed on VARIAN Cary 5000 and Cary Eclipse spectrophotometers, respectively. Scanning electron microscopy (SEM) was performed on the Phenom Pharos G2 instrument. The phosphorescence decay curve was measured using a FLS920 fluorescence spectrometer (Edinburgh Instruments Ltd. UK). Cyclic voltammetry tests and corresponding calculations were described in the previously reported literature.[1]

Single crystal preparation and X-ray crystallography test: 20 mg of BBPED dissolved in dichloromethane/petroleum ether (4 mL/8 mL) and left to stand at 298 K for 10 days. Subsequently, the single crystal was performed on the Bruker APEX-II CCD diffractometer (MoKα, λ = 0.71073 Å) at 273.15 K (CCDC number: 2194270).

Frontier molecular orbital, TD-DFT, growth morphology, energy framework, and Hirshfeld surface calculations. Nanoindentation and powder X-ray diffraction measurements were reported in our previous report.[2]

Accession Codes. CCDC 2194270 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting. The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

Table S1. Photophysical data of **BBPED**

Compound	Absorption[a] (nm) ($\varepsilon/\times10^4$ $M^{-1}cm^{-1}$)		Emission[b] (nm)		HOMO (eV)[c]	LUMO (eV)[d]	E_g (eV)[e]
TFMAC	cyclohexane 262 nm (1.09) 301 nm (0.24)	microcrystal 292 nm 409 nm	cyclohexane 473 nm 502 nm	microcrystal 545 nm	-7.36	-3.53	3.83

[a] Maximal absorption peak in cyclohexane (1.0×10^{-5} M) and microcrystal.

[b] Maximal emission peak in cyclohexane (1.0×10^{-5} M) and microcrystal.

[c] Electrochemical method was used to obtain the HOMO energy levels by comparing with an external reference, the ferrocene/ferrocenium (F_c/F_c^+, 4.8 eV relative to vacuum).

[d] The LUMO energy level was estimated by the equation: $E_{LUMO} = E_{HOMO} + E_g$.

[e] E_g was determined from the edge of the absorption spectrum.

Table S2. Main electronic transitions calculated with TD-DFT

λ_{abc}[a] (nm)	f[b]	Transition (%)[c]
289.94	0.2697	H-3 → L (94.1)
259.35	0.0024	H-5 → L (57.1) H-7 → L (23) H-9 → L (8.4) H → L+1 (2.4)

[a]Experimental absorption in cyclohexane; [b]Compound oscillator strength; [c]H represent HOMO, L represent LUMO.

Table S3. The hardness (*H*) and elasticity modulus (*E*) in the single crystal (002) face of **BBPED**

Mechanical properties	1	2	3	Average value
H, GPa	0.131307	0.166249	0.193398	0.16±0.02
E, GPa	5.010381	5.428938	6.318297	5.58±0.54

Table S4. Single crystal data of **BBPED**

	BBPED
formula	$C_{14}H_8Br_2O_2$
formula weight	368.02
temperature/k	273.15
space group	I2/c
crystal system	monoclinic
a (Å)	12.1441(18)
b (Å)	4.0992(6)
c (Å)	25.880(4)
α (deg)	90
β (deg)	95.771(7)
γ (deg)	90
V ($Å^3$)	1281.8(3)
Z	4
dcalc(g/cm^3)	1.907
μ (mm^{-1})	6.313
F(000)	712.0
radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.33 to 54.944
index ranges	$-15 \le h \le 15$, $-5 \le k \le 5$, $-33 \le l \le 33$
reflections collected	23915
independent reflections	1472 (R_{int} = 0.0804, R_{sigma} = 0.0328)
data/restraints/parameters	1472/0/82
final R indexes (I> = 2σ(I))	R_1 = 0.0486, wR_2 = 0.1017
final R indexes (all data)	R_1 = 0.0693, wR_2 = 0.1104
largest diff. peak/hole / e $Å^{-3}$	0.68/-0.39
goodness-of-fit on F^2	1.144
CCDC	2194270

Table S5. Stabilization energies (kJ/mol) of the individual molecular pairs associated with different intermolecular interactions

Number	Symmetry operation	R[a], Å	Electron density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}[b]
1	x, y, z	4.10	HF/3-21G	-10.2	-1.9	-71.4	32.9	-49.4
2	-x, -y, -z	13.55	HF/3-21G	-1.6	-0.3	-5.8	1.4	-5.9
3	x+1/2, y+1/2, z+1/2	13.88	HF/3-21G	-1.4	-0.1	-5.2	4.7	-2.3
4	-x+1/2, -y+1/2, -z+1/2	6.38	HF/3-21G	-0.9	-2.2	-23.5	9.8	-15.7
5	-x, -y, -z	12.94	HF/3-21G	-4.2	-0.5	-12.8	7.6	-10.0
6	-x+1/2, -y+1/2, -z+1/2	6.43	HF/3-21G	-18.7	-4.2	-23.6	10.3	-34.7

[a] The distance between molecular centroids (mean atomic position). [b] Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately.

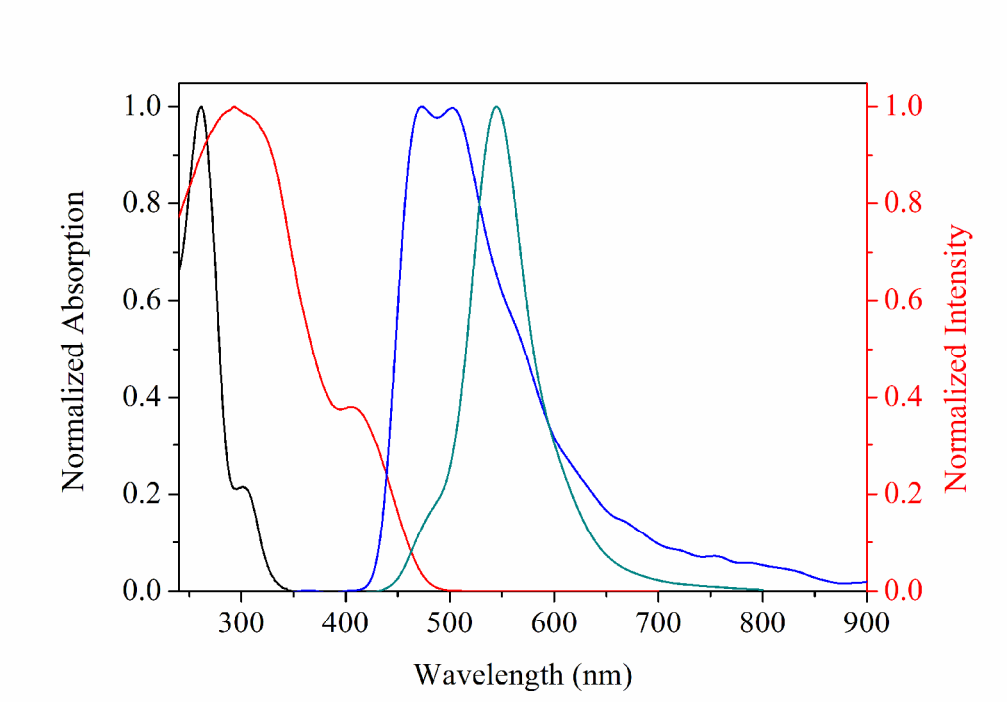

Figure S1. Normalized UV-vis absorption (black line, cyclohexane, red line, microcrystal) and fluorescence emission (blue line, cyclohexane, green line, microcrystal) spectra (λ_{ex} = 300 nm) of **BBPED** in cyclohexane (1.0×10^{-5} M) and microcrystal.

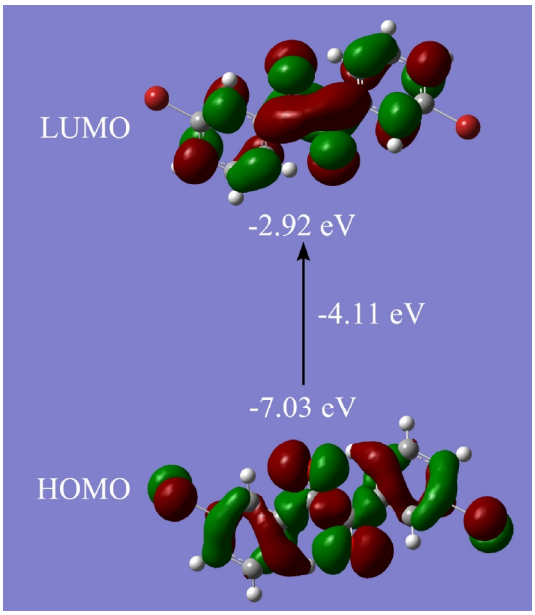

Figure S2. The frontier orbital plots of HOMO and LUMO of the **BBPED**.

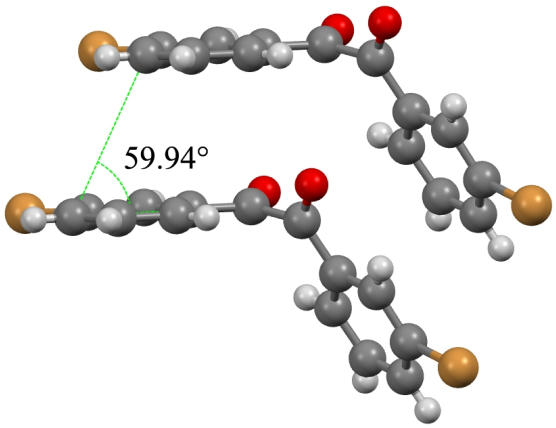

Figure S3. *J*-aggregation of **BBPED** molecules in crystal.

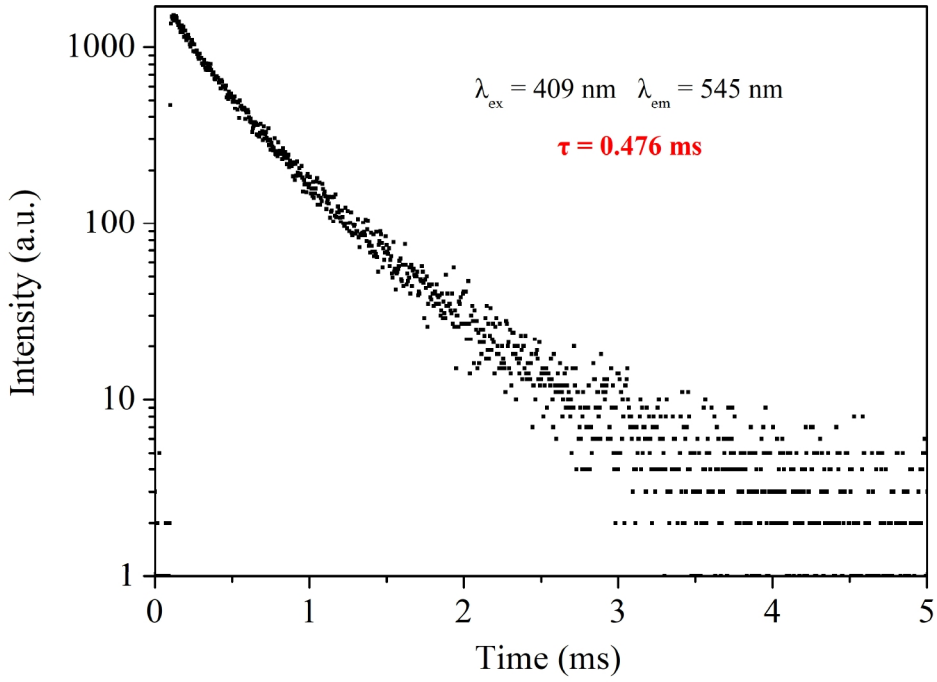

Figure S4. Phosphorescent decay curve of **BBPED** crystal measured at 545 nm.

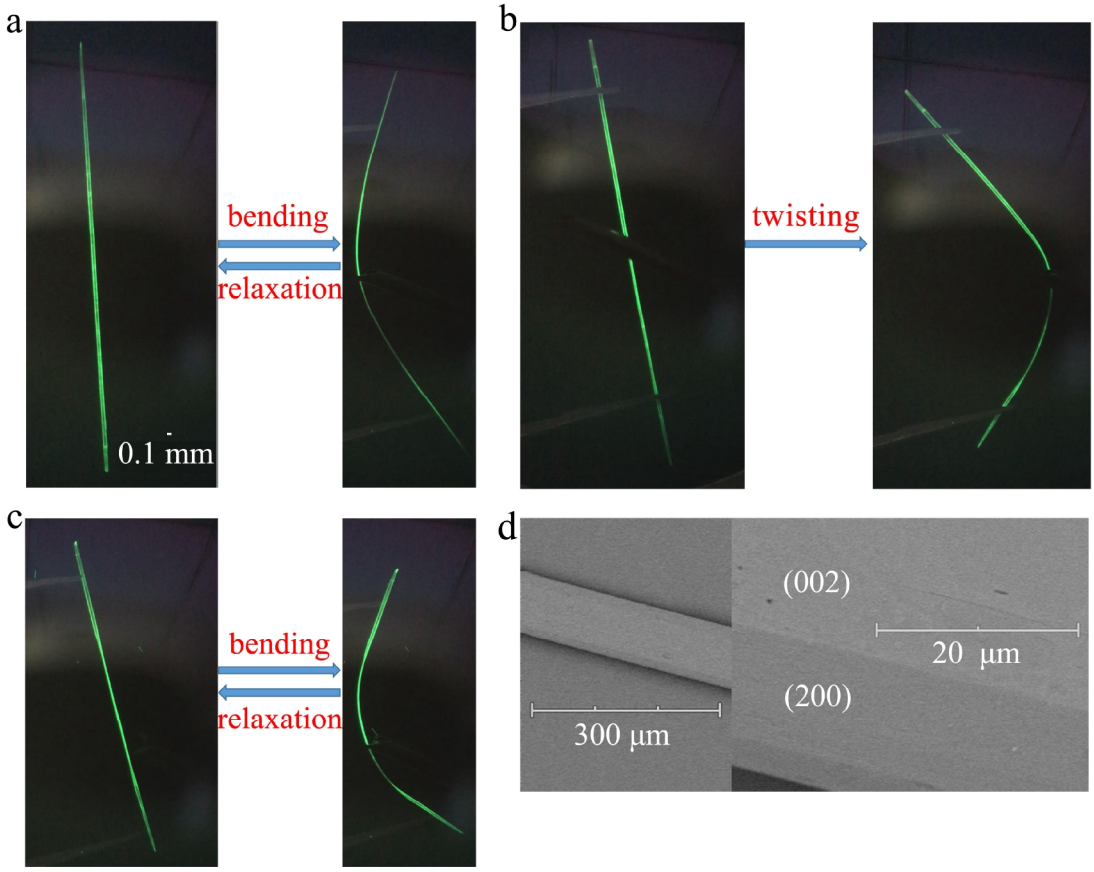

Figure S5. Elastic bending (a), plastic twisting (b) and elastic bending after twisting (c) pictures of the **BBPED** crystal (green, 10.42mm×0.11mm×0.018mm, 298 K); SEM pictures of the crystal (d).

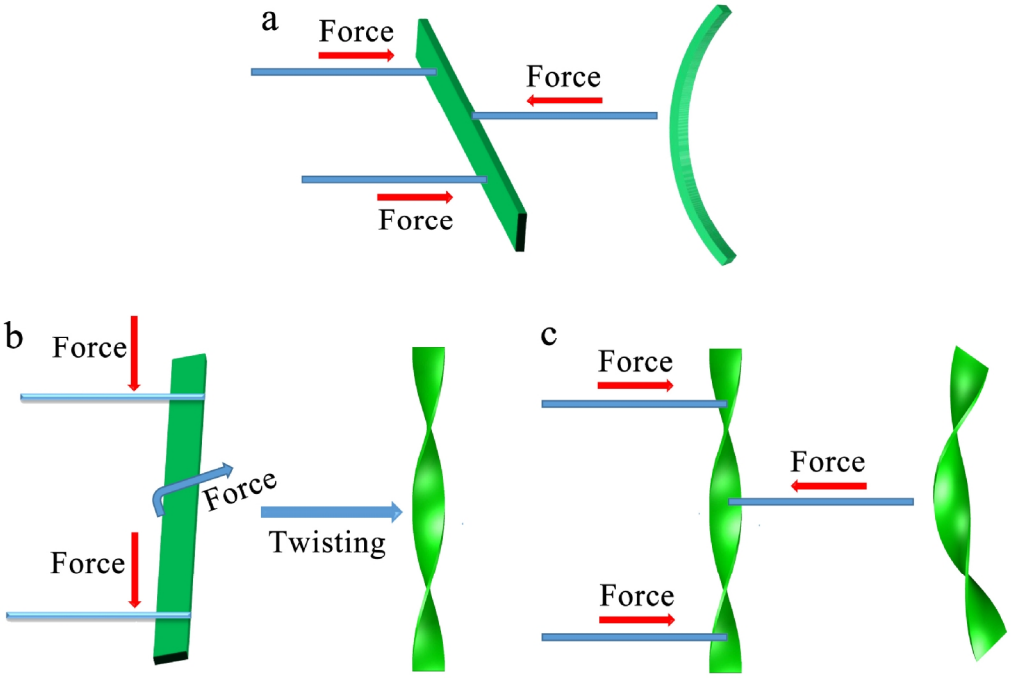

Figure S6. Force pictures of crystal elastic bending (a), plastic twisting (b) and elastic bending after twisting (c).

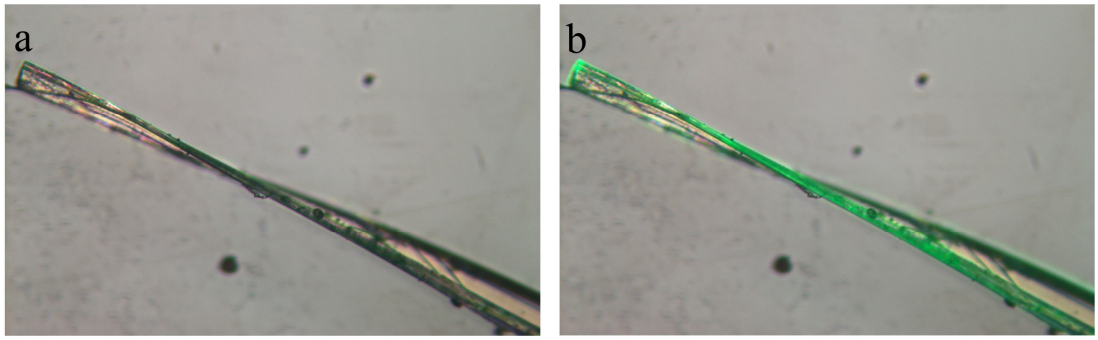

Figure S7. High resolution microscope photos of twisted crystals under visible light (a) and 365 nm light (b).

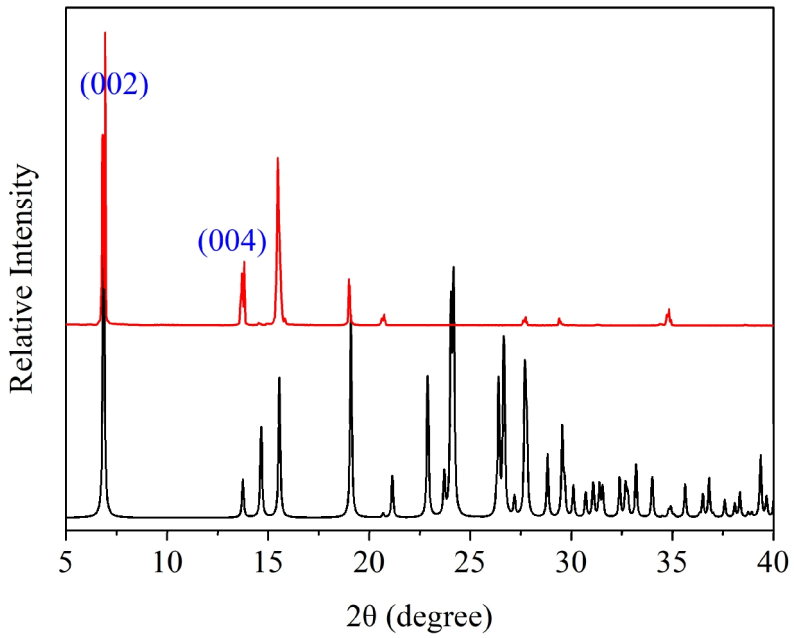

Figure S8. PXRD data from actual test (red line) and simulation (black line) of **BBPED** crystal.

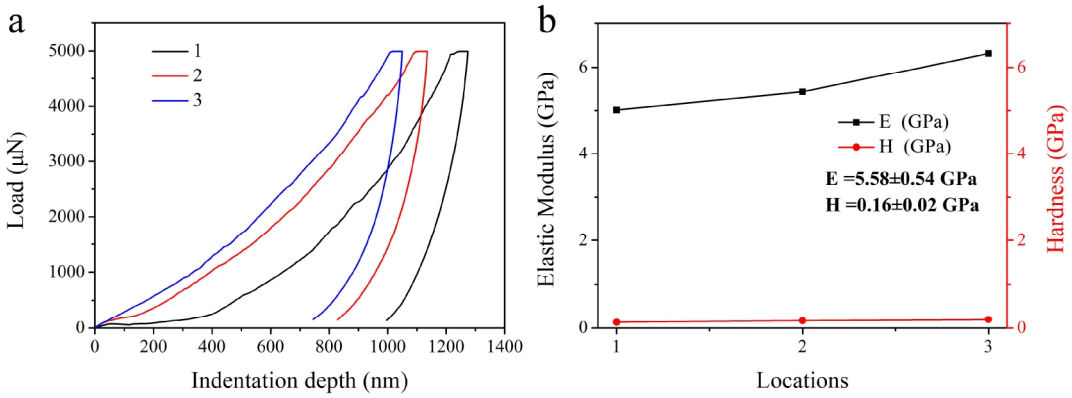

Figure S9. The load-depth curves (a), elastic modulus and hardness (b) for the (002) face of the **BBPED** crystal.

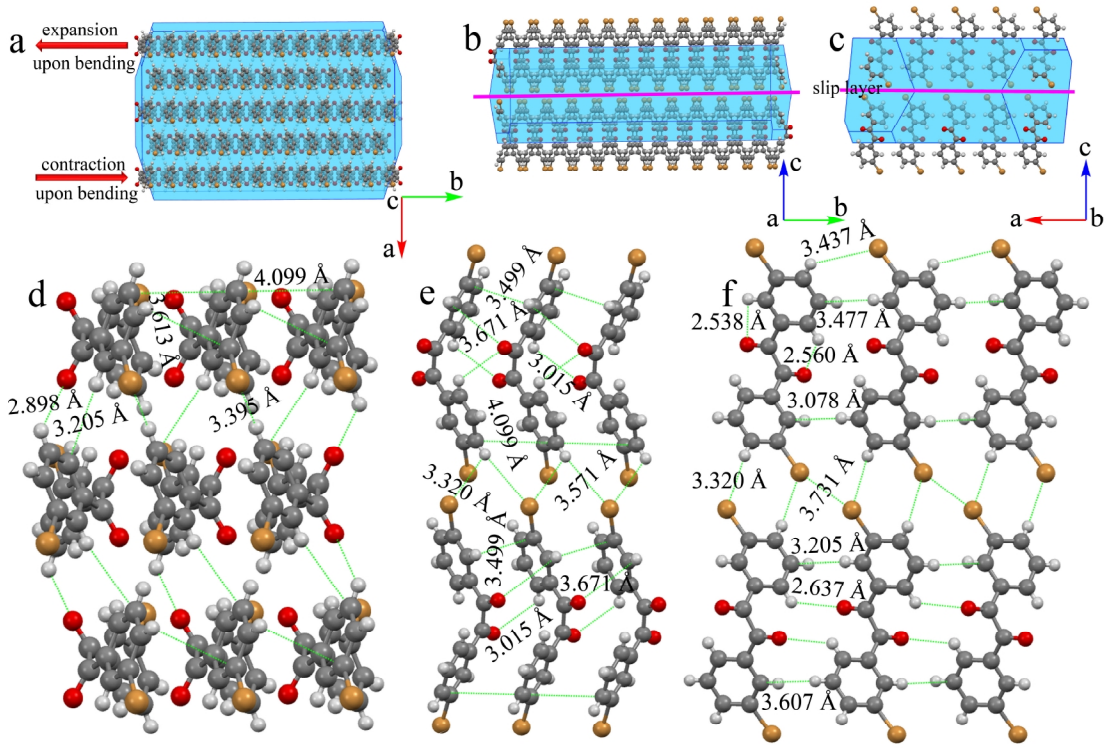

Figure S10. Simulated molecular packing mode (a, b, c) and intermolecular interactions (d, e, f) viewed along the (002), (200) and (020) faces (C, H, O, Br correspond to gray, white, red, and yellow atoms).

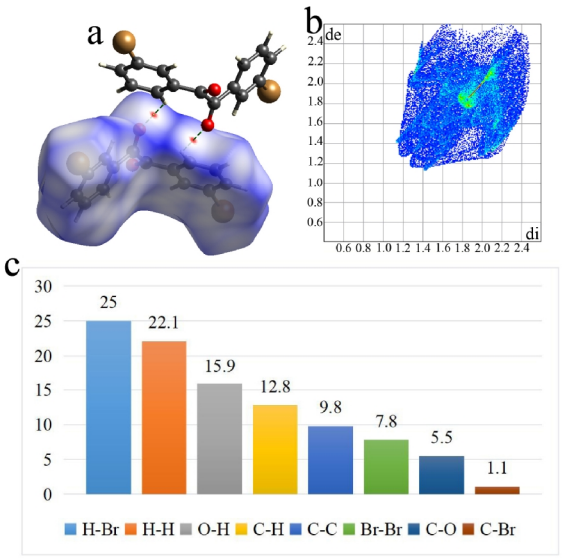

Figure S11. Hirshfeld surfaces mapped over d_{norm} of **BBPED** (a) with d_e (left) and d_i (right) mapped in colour (in both cases red represents the closest contacts, and blue the most distant contacts); 2D fingerprint plots produced from the two functions for **BBPED** (b); The percentage of individual atomic contact contributions to the Hirshfeld surface for **BBPED** (c).

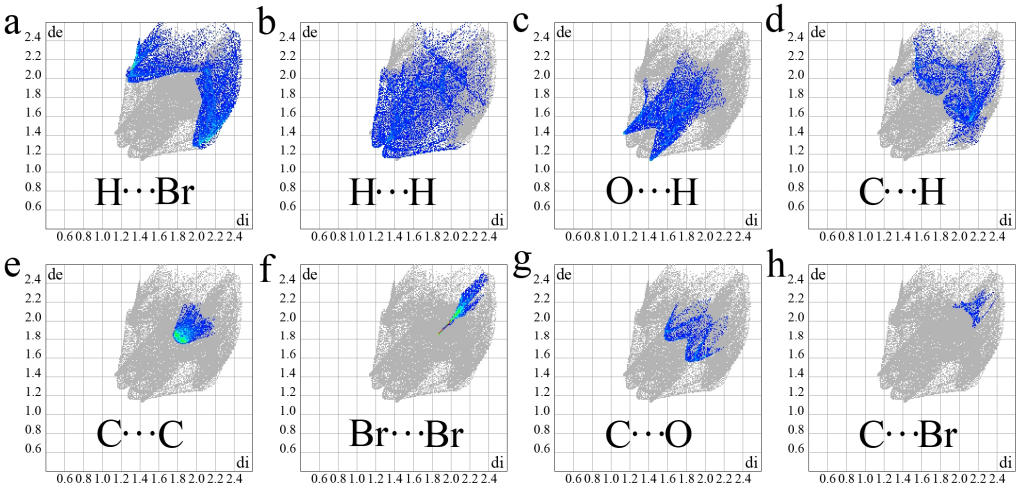

Figure S12. 2D fingerprint plots produced from the H-Br (a), H-H (b), O-H (c), C-H (d), C-C (e), Br-Br (f), C-O (g) and C-Br (h) intermolecular interactions of **BBPED**.

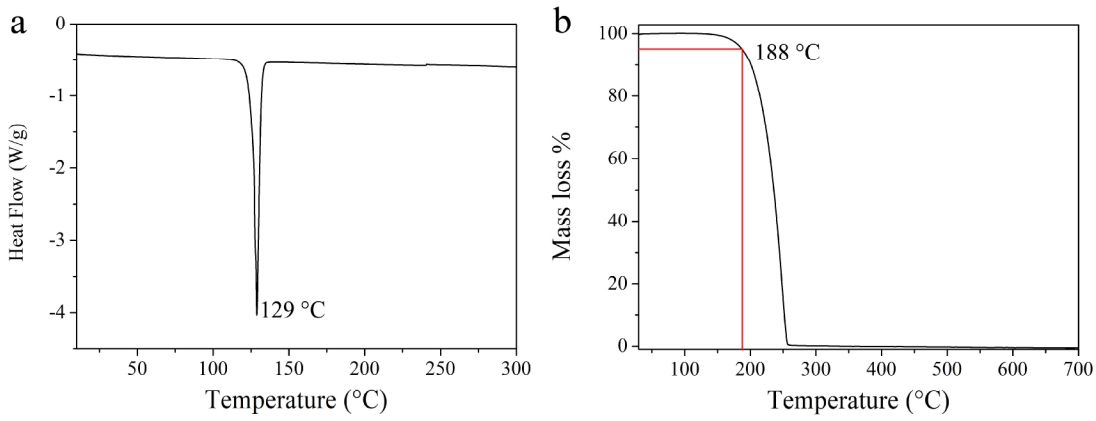

Figure S13. The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) traces of **BBPED**.

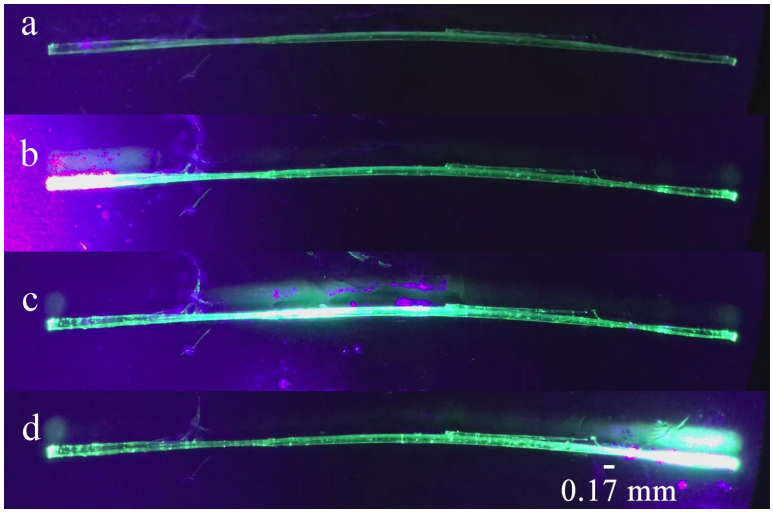

Figure S14. Image of twisted crystals (green, 5.5mm×0.17mm×0.04mm, 298 K) excited at 365 nm light (a, before excitation, b-c, excitation at different positions).

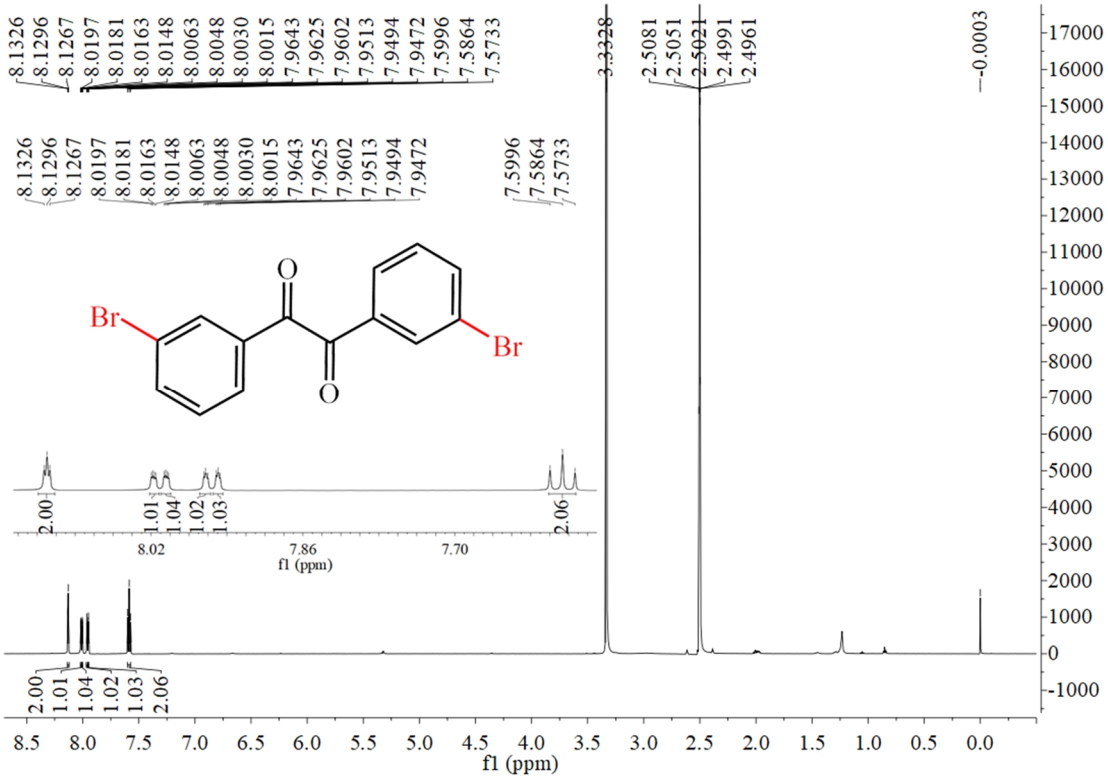

Figure S15. ^{1}H NMR (600 MHz) spectrum of **BBPED** in DMSO-d_6.

n REFERENCES

(1) Zhang, T.; Han, Y. N.; Liang, M.; Bian, W. X.; Zhang, Y.; Li, X. T.; Zhang, C. Y.; Xue, P. C. Substituent effect on photophysical properties, crystal structures and mechanochromism of D-π-A phenothiazine derivatives. *Dyes Pigm*. **2019**, 171, 107692.

(2) Peng, J.; Han, C. C.; Bai, J. K.; Wang, J. Z.; Cao, X. M.; Jia, J. H.; Wang, Y. F.; Wu, J. N. Organic single crystal/polymer hybrid actuator with waveguide, low temperature, and humidity actuation properties. *Cryst. Growth Des.* Doi. org/10.1021/acs.cgd.2c00855.