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Supporting information for article:

Polymorphs of 2,4,6-tris(4-pyridyl)-1,3,5-triazine and their mechanical properties

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Table S1 Comparison of the two phases of TPT-I and TPT-II.

	TPT-I (Janczak *et al*., 2003)	TPT-II (this work)
Chemical formula	$C_{18}H_{12}N_6$	$C_{18}H_{12}N_6$
Space group	*C*2/*c*	*I*2/*a*
a, *b*, *c* (Å)	13.027(2), 11.155(2), 10.796(2)	21.3126(18), 3.7347(2), 35.187(2)
β (°)	111.50 (2)	93.367 (7)
V (Å^3)	1459.67	2795.9 (3)
Z	4	8
D_{calc} (g cm^{-3})	1.421	1.484
μ (mm-1)	0.091	0.100
Crystal size (mm)	0.38 × 0.32 × 0.28	0.79 × 0.07 × 0.03
Melting point (°C)	406-407	390-391

Table S2 CH···N hydrogen bonds in TPT-II.

	d(C-H) /Å	*d*(H···N) /Å	*d*(C···N) /Å	∠(CH···N) /º
C10-H10···N4^{i}	0.96(3)	2.57(3)	3.497(3)	161(2)
C11-H11···N5^{ii}	0.98(2)	2.67(2)	3.522(3)	144.7(18)
C17-H17···N6^{iii}	0.96(3)	2.69(3)	3.521(3)	144.6(18)
C18-H18···N4^{i}	0.93(3)	2.61(3)	3.466(3)	154(2)

Note: ^{i} = 1/2+x, 1-y, z; ^{ii} = 3/2-x, 1/2-y, 1/2-z; ^{iii} = 3/2-x, y, 1-z.

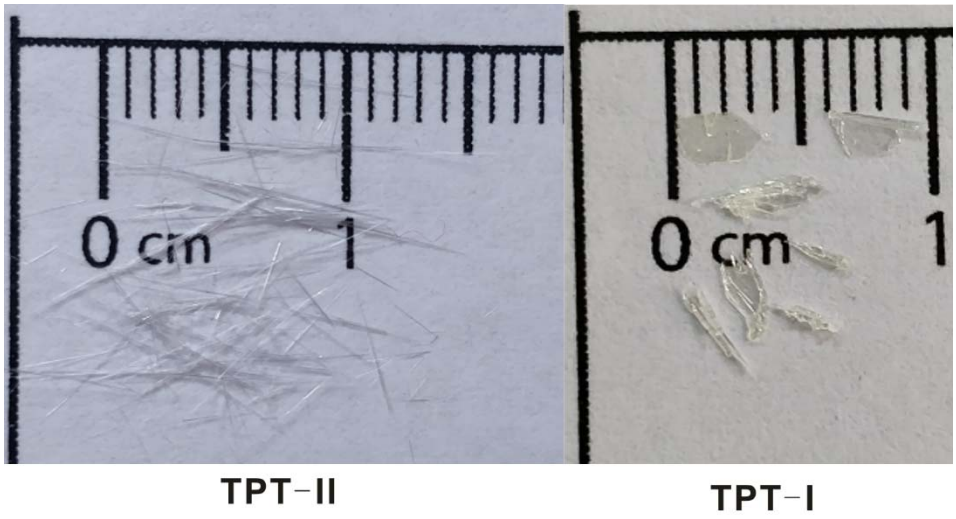

Fig. S1. The photos for the single crystals of TPT-II (left) and TPT-I (right) with scale bar.

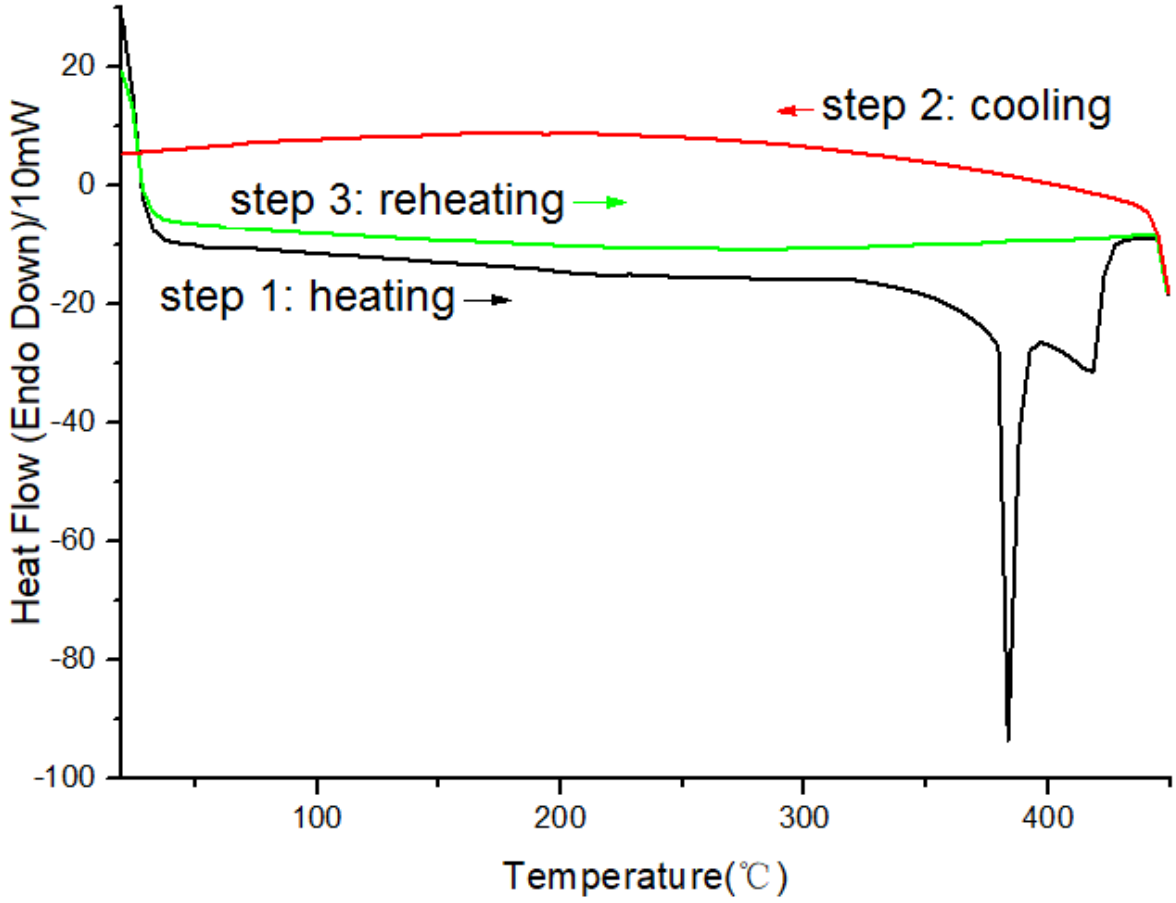

Fig. S2 The DSC curves starting from the crystalline powder of TPT-II. The heating and cooling rates are at 10 °C/min. The sharp endothermic peak at around 390 °C indicates the melting point of TPT-II. No obvious endo- or exo-thermic signals in step 2 and step three

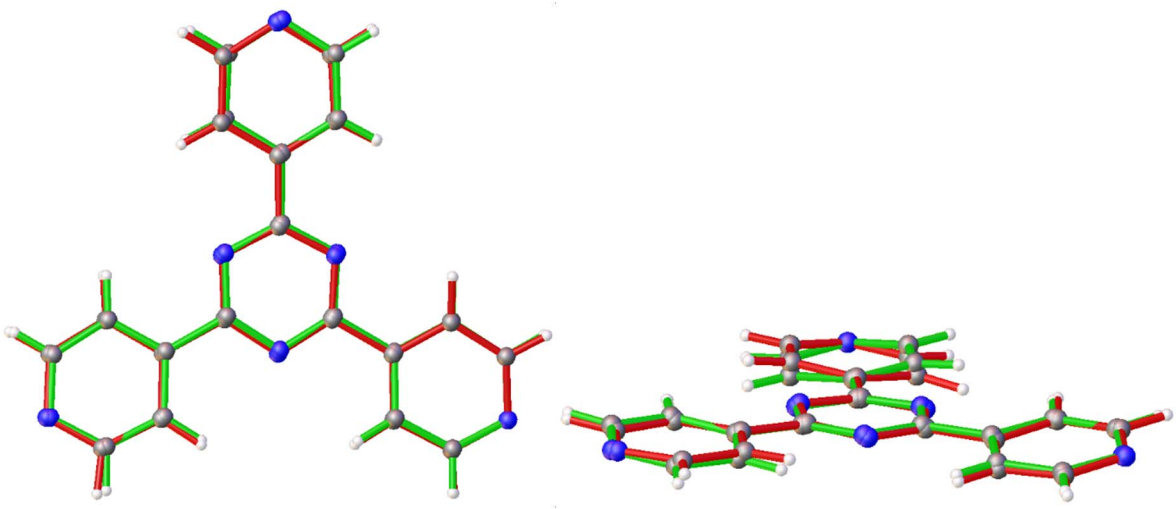

Fig. S3 Different views of the structural comparison of TPT-I (in green) and TPT-II (in red). The molecules were overlaid using the "Overlay Structure" tool in Olex2 (Version 1.2.8; Dolomanov *et al.*, 2009).

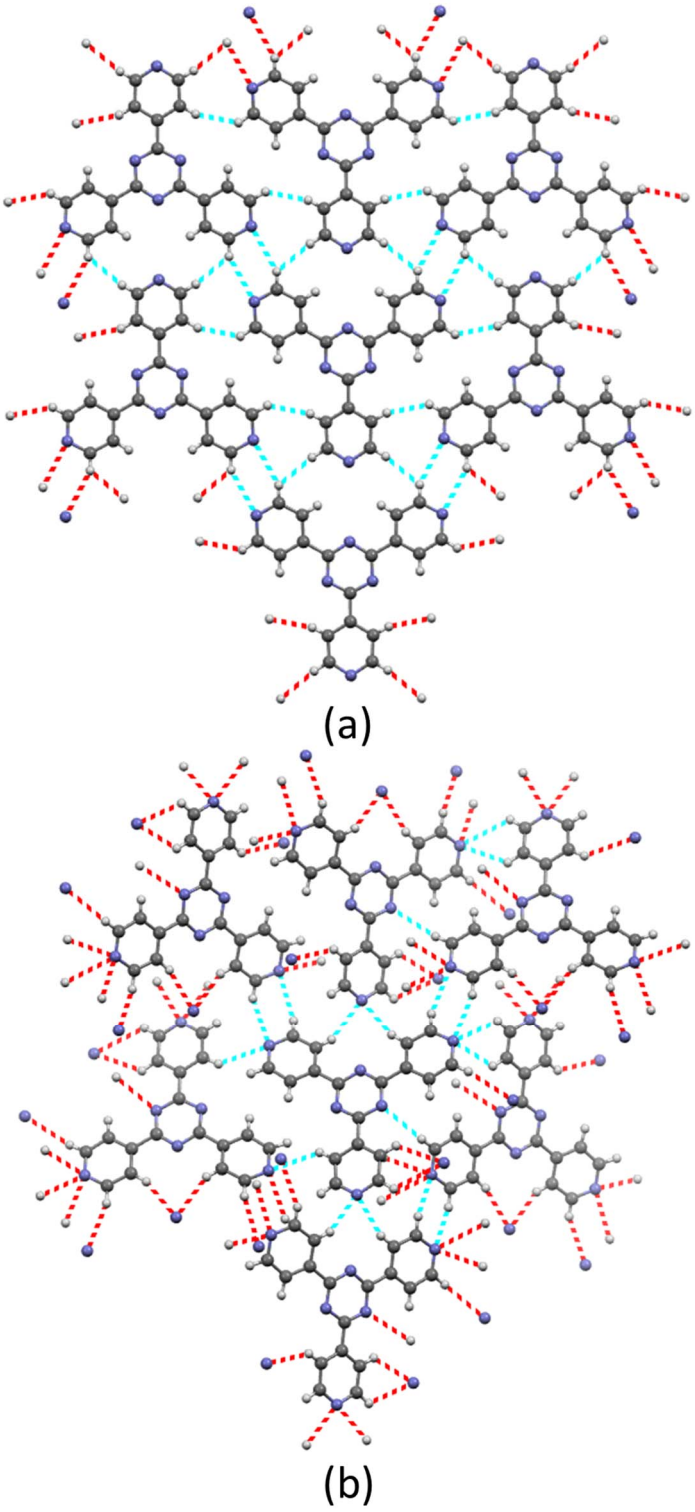

Fig. S4 The intermolecular contacts in the layer perpendicular to the π···π stacking direction in TPT-I (a) and TPT-II (b). The intermolecular interactions were shown as dashed lines.

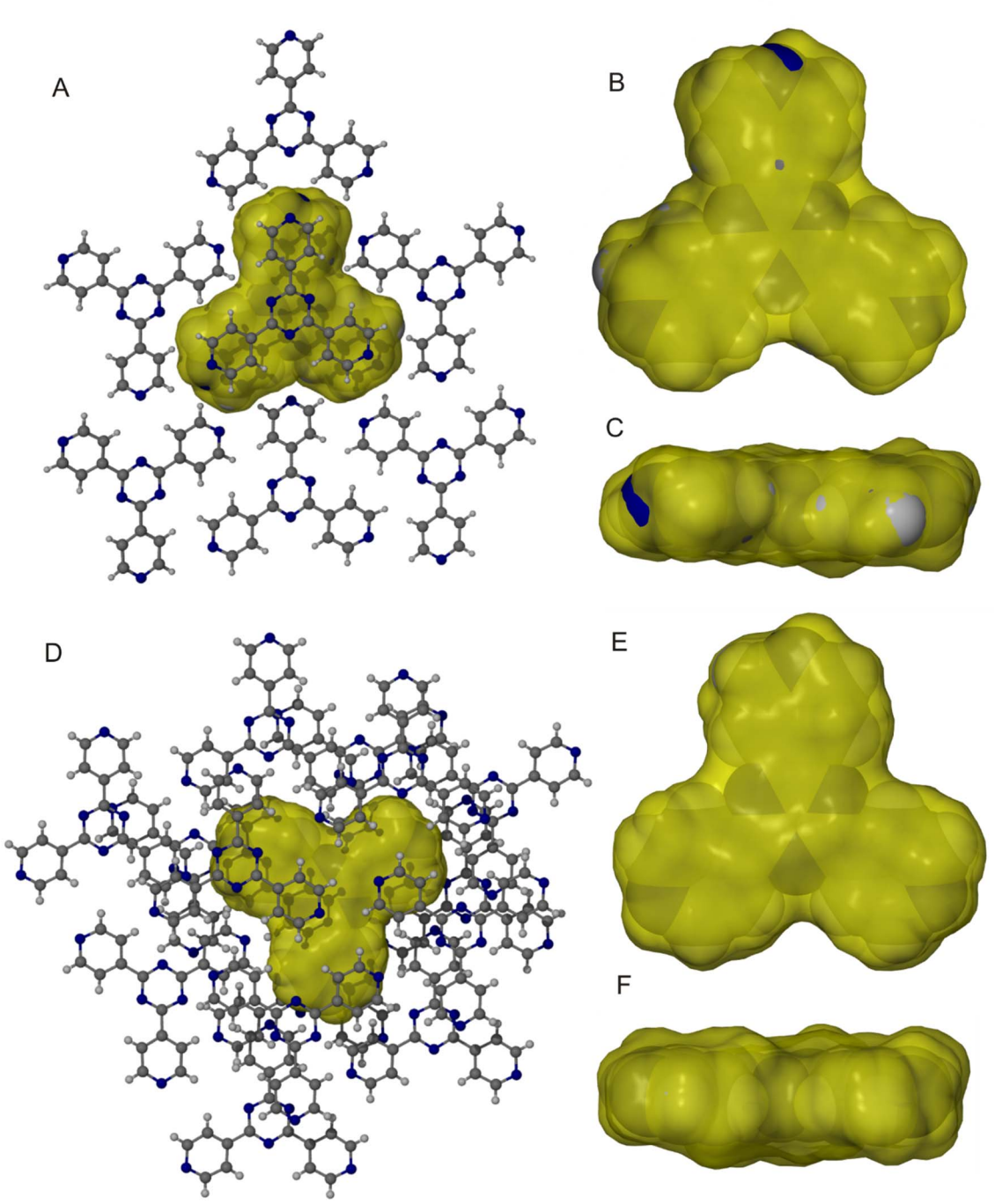

Fig. S5 The molecular volume mapped with Connolly surface (Connolly, 1993) with probe radius of 1.2 Å for TPT-I (A, B, C) and TPT-II (D, E, F).

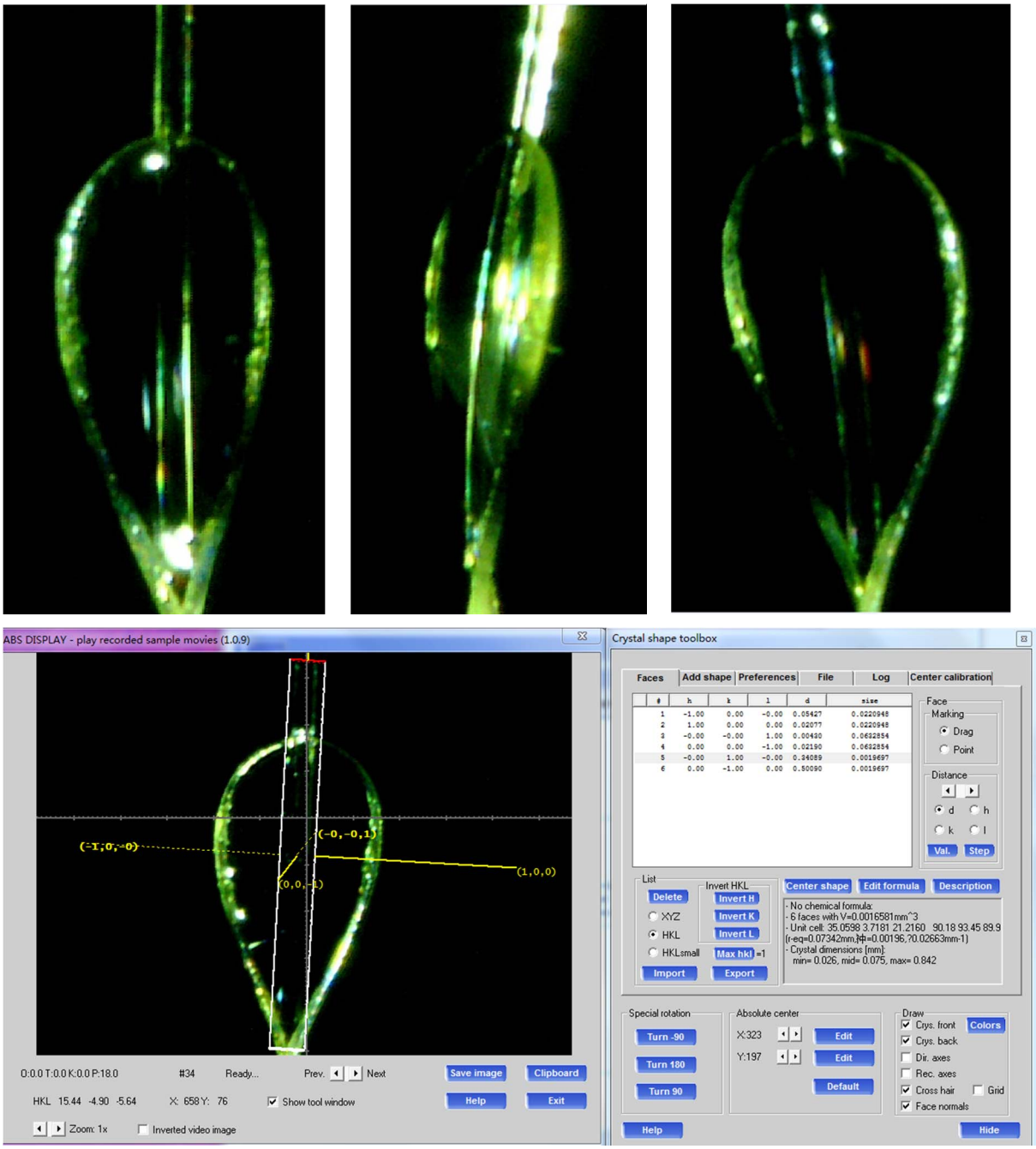

Fig. S6. Pictures of the single crystal mounted on the diffractometer and the face indexed image with CrysAlisPro (Rigaku OD, 2018).

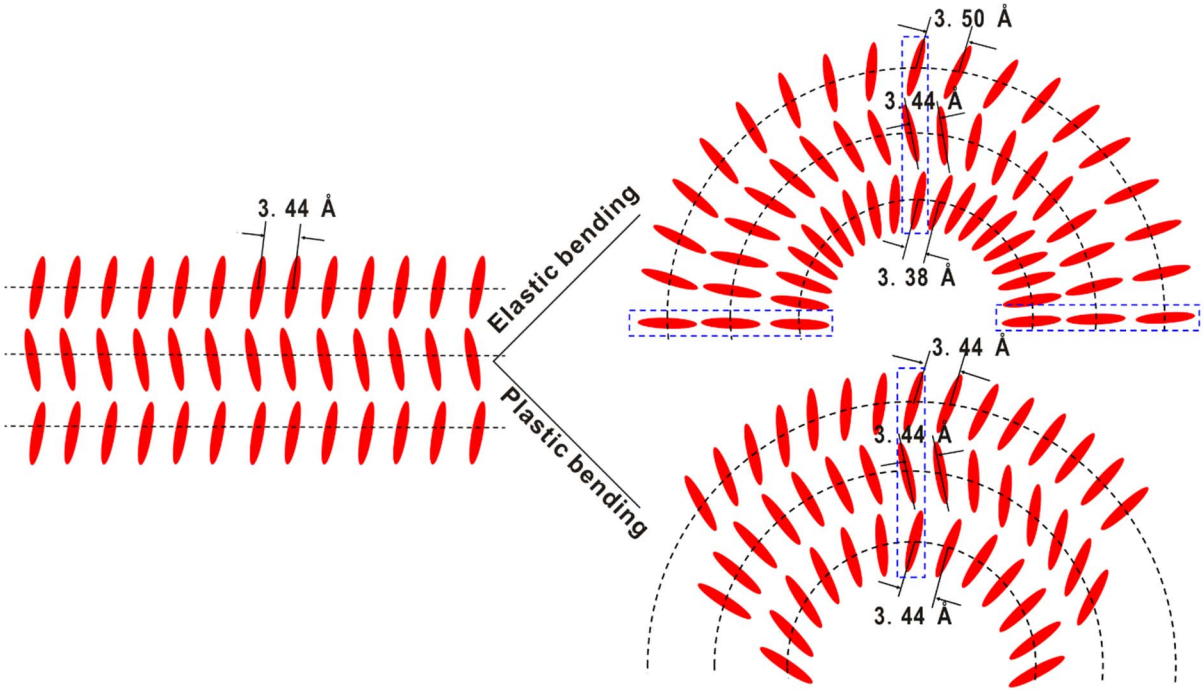

Fig. S7 The rough π···π distances before (left) and during elastic bending (right top) of the crystal, calculated based on the rod needle crystal with the length of 0.344 cm (ca. 10^7 molecules in a line) and diameter of 0.04 mm. During plastic bending (right down), the π···π stacking columns (layers) slide thus the π···π distances don't change significantly.

Note: Assume the size of the single crystal is 3.44 mm long with radius of 0.04 mm (consistent with the real single crystals), and the relative position of the molecules vertical to the *b* axis doesn't change (no slippage of the π···π stacking column). According to the centroid-to-centroid distance of 3.44 Å in the structure, there exist 10^7 TPT molecules along the *b* axis direction. When such a crystal bends forming a semicircle, r_{outer} would be 0.02 mm (0.5*0.04 mm) longer than the radius of the straight crystal, while the r_{inner} would be 0.02 mm shorter. Then the lengths of the outer and inner columns are expanded and compressed by around 0.06 mm (0.02*π), respectively. The distance change between the neighbouring TPT molecules is ca. 0.06 Å if the 0.06 mm is distributed averagely over the 10^7 TPT molecules, resulting in the π···π distances at the outer and inner columns at ca. 3.50 and 3.38 Å, respectively. The fact that the thicker crystals (eg. 0.2 mm in radius) are easily broken for the mechanical property test also verify the above inference.

References:

Connolly, M. L. (1993) *J. Mol. Graphics*, **11**, 139-141.

Janczak, J., Śledź, M., & Kubiak, R. (2003). *J. Mol. Struct.* **659**, 71-79.

Rigaku Oxford Diffraction (2018). *CrysAlisPro*, version 1.171.39.46e.