Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

Straight, bendable and bent organic crystals

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Experimental Section

All solvents and reagents were commercially available and used as received without further purification. Bruker D8 Venture Single Crystal X-ray Diffractometer (SCXRD) was used for collecting intensity data of single crystals at 100(2) K. Powder X-ray diffraction (PXRD) analysis were performed on a D5005 Siemens X-ray diffractometer with graphite monochromatized CuKα radiation (λ = 1.54056 Å) at RT (298 K). The PXRD of the bendable crystals was obtained by keeping the bulk of the crystals on the sample holder without grinding them, to get an idea of the most preferred orientation of the crystals. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DRX 400 spectrometer with TMS as an internal reference in DMSO-d_6 solution. The elemental analyses (C, H, N) were carried out by using ElementarVario Micro Cube instrument at the Elemental Analysis Lab, CMMAC, Department of Chemistry, National University of Singapore. All UV-irradiation experiments were conducted in a LUZCHEM 4V UV reactor (wavelength 350 nm).

Synthesis of 4-phenylazobenzoic acid, pab, 1. pab was synthesized using the reported literature.[1] 4-aminobenzoic acid (1.00 g, 0.007 mmol) was dissolved in 40 mL warm glacial acetic acid. The solution was cooled to room temperature, nitrosobenzene (0.781 g, 0.007 mmol) was added and the mixture was stirred overnight in the dark. The yellow precipitate formed was collected on a Buchner funnel and washed with acetic acid and water. The precipitate was air dried and recrystallized in a methanol solution to obtain orange-yellow plates of single crystals. Yield: 41%. ^{1}H NMR (400 MHz), DMSO-d_6, 298 K: δ = 13.18 (s, 1H, H of –COOH), 8.13-8.16 (d, 2H, H adjacent to COOH group), 7.92-7.98 (m, 4H, H surrounding -N=N- group), 7.61-7.65 (m, 3H, Ph-H of pab). Elemental Analysis for $C_{13}H_{10}N_2O_2$ (MW: 226.23): Calculated: C: 69.02, H: 4.46, N: 12.38; Found: C: 68.99, H: 4.56, N: 12.28;

Recrystallization of thin films of pab, 2. Crystals of pab (4 mg, 0.001 mmol) were dissolved in a DCM/EtOH (2:1 v/v) solution in a beaker and kept for slow evaporation in the absence of light. After complete evaporation, both long crystals and long thin films could be observed. Elemental Analysis for $C_{13}H_{10}N_2O_2$ (MW: 226.23): Calculated: C: 69.02, H: 4.46, N: 12.38; Found: C: 68.99, H: 4.49, N: 12.36;

Recrystallization of bent crystals of pab, 3. Crystals of pab (4 mg, 0.001 mmol) were dissolved in a DCM/EtOH (2:1 v/v) solution (total 1.5 mL) in a vial (20 mL). The vial was capped and kept in a UV reactor LUZCHEM 4V (352 nm) for 15 min. The vial was uncapped and left undisturbed for recrystallization in the dark. The bent crystals were obtained in majority, along with few straight plates in the same vial. ^{1}H NMR (400 MHz), DMSO-d_6, 298 K: δ = 13.18 (br, 2H, H of –OH), 8.13- 8.17 (d, 2H, H adjacent to COOH group in *trans*-pab), 7.92- 7.99 (m, 4H, H surrounding –N=N- group of *trans*-pab), 7.82- 7.85 (d, 2H, H adjacent to COOH of *cis*-pab), 7.28-7.33 (t, 2H, Ph-H of *cis*-pab), 7.62- 7.64 (m, 3H, Ph-H of *trans*-pab), 7.18 (t, 1H, Ph-H of *cis*-pab), 6.92- 6.95 (d, 2H, H of Ph-COOH of *cis*-pab), 6.85- 6.88 (d, 2H, Ph-H of *cis*-pab). Elemental Analysis for $C_{13}H_{10}N_2O_2$ (MW: 226.23): Calculated: C: 69.02, H: 4.46, N: 12.38; Found: C: 68.98, H: 4.56, N: 12.35;

Table S1. Crystallographic information of straight crystals and thin films of pab

Compound	Straight crystals (100K)	pab films (298 K)
Empirical Formula	$C_{13}H_{10}N_2O_2$	$C_{13}H_{10}N_2O_2$
Molecular weight (g mol^{-1})	226.23	226.23
Crystal System	Monoclinic	Monoclinic
Space Group, Z	$P2_1/c$, 4	$P2_1/c$, 4
a (Å)	5.6324 (4)	5.7116(3)
b (Å)	30.062 (2)	30.6725(3)
c (Å)	6.7574 (6)	6.8191(8)
α (°)	90.0	90.0
β (°)	111.203(3)	111.699 (7)
γ (°)	90.0	90.0
V (Å^3)	1066.72(15)	1109.976 (53)
D_{calc} (g cm^{-3})	1.409	
μ (mm-1)	0.097	
GOF	1.067	
R1	0.0781, 0.0525	
wR2	0.1357, 0.1235	
Total reflections	2649	
Unique reflections	1986	

CCDC number for **1**: 1956732

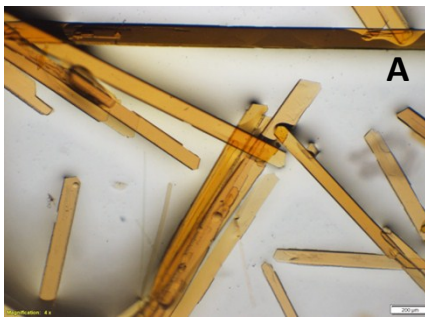


Fig S1. Microscopic images of straight crystals, **1**.

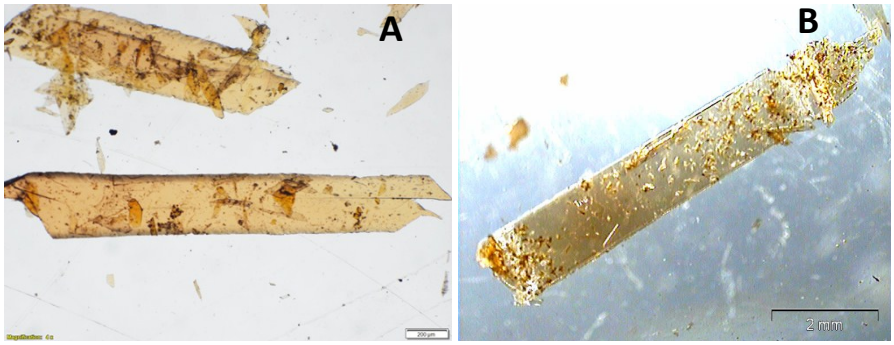


Fig S2. Microscopic images of bendable crystals, **2**.

Fig S3. Microscopic images of bent crystals, **3**.

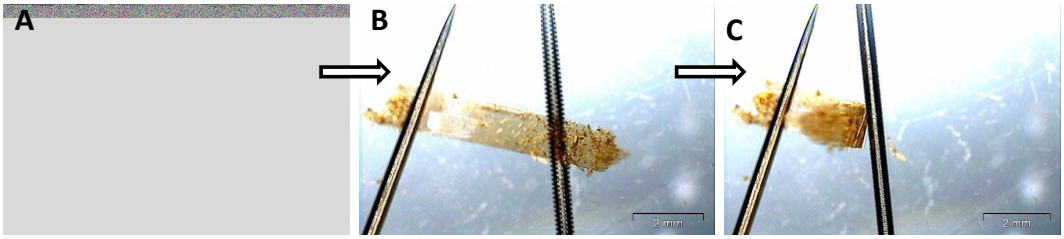


Fig S4A. A macroscopic pab film, **2** was mechanically bent using a pair of needles to check its elastic bendability (A-C).

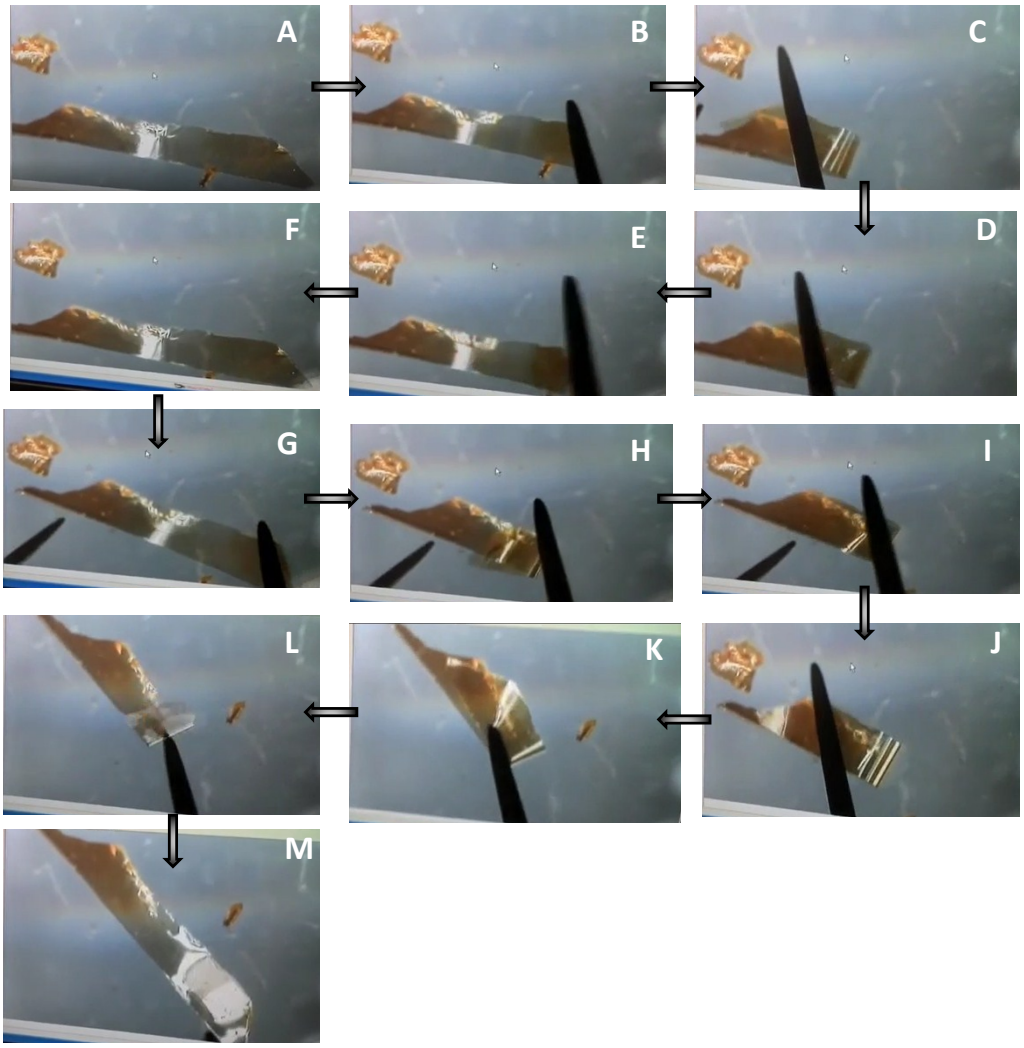


Fig S4B. A macroscopic pab film, **2** was mechanically bent using a pair of needles to check its elastic bendability (A-M).

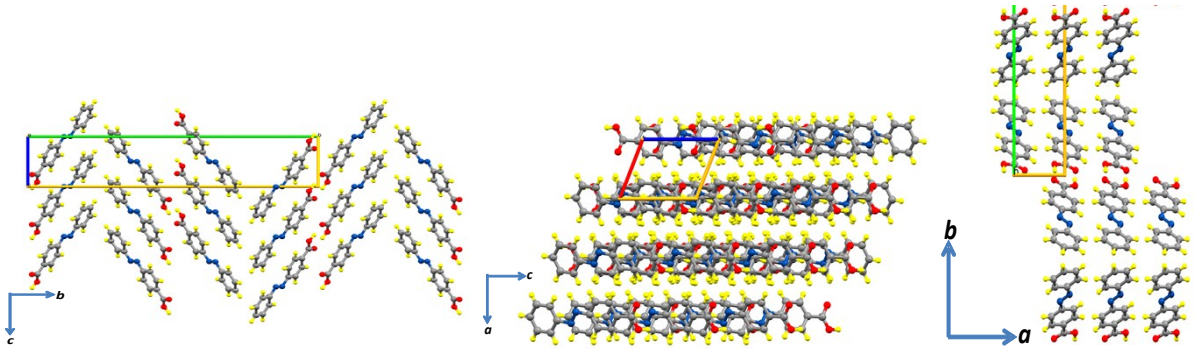


Fig S5. Packing of pab film, **2** viewed in projection down the *a*, b, c axes respectively.

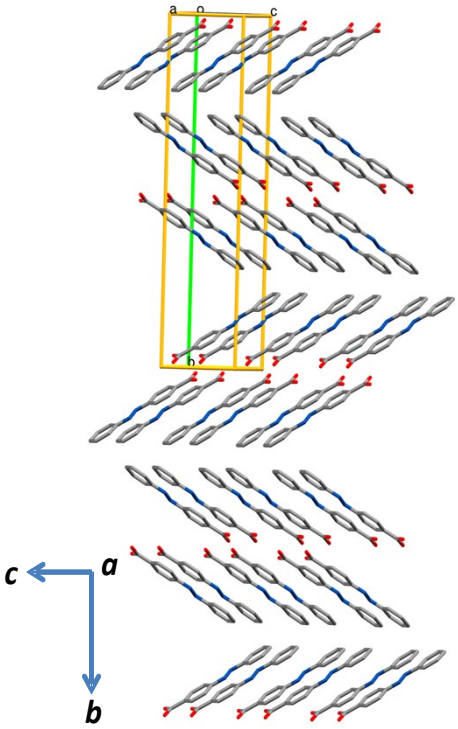


Fig S6. Molecular packing structure of **2**, viewed down the (010) face in projection along the *b* axis, showing a crisscross arrangement of columns of molecules of PAB preventing the long- range sliding of molecules and hence imparting the elastic bending property. The molecules within the same column are stabilized by π···π interactions.

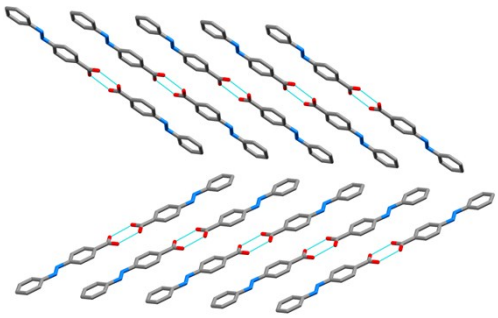
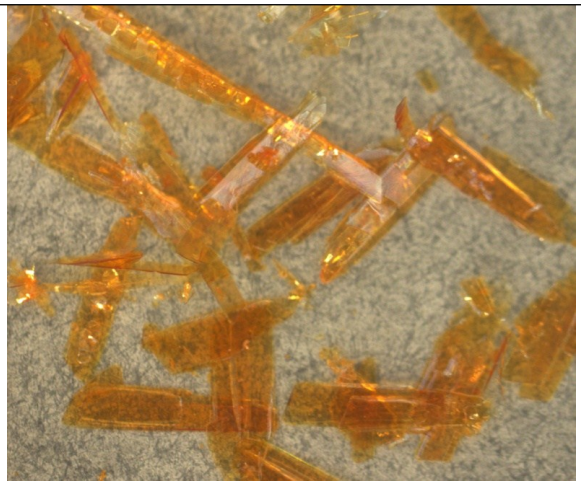
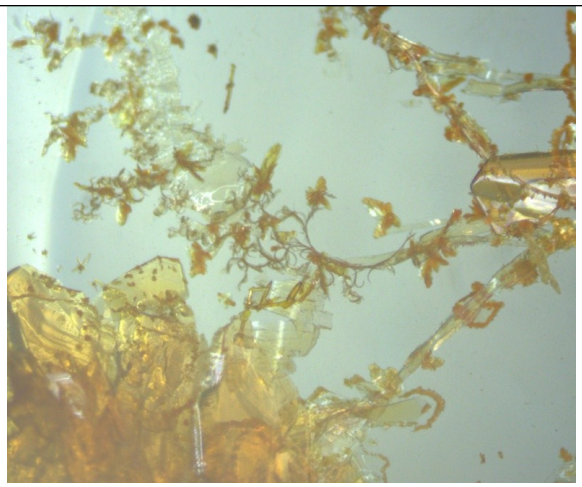
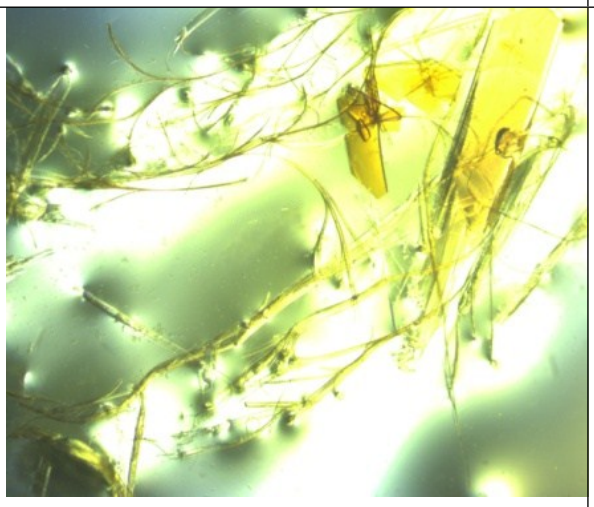
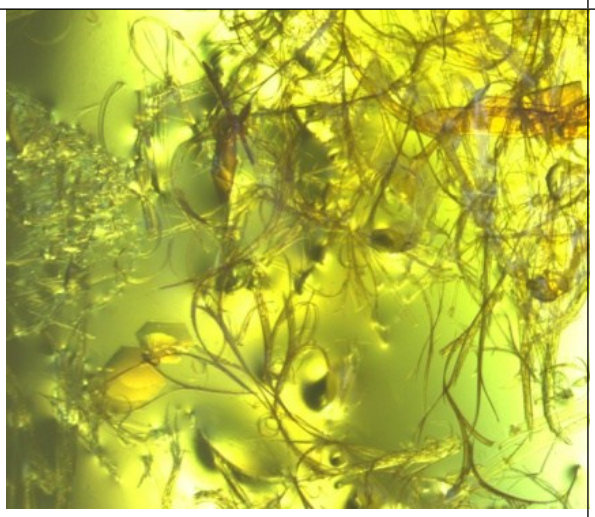
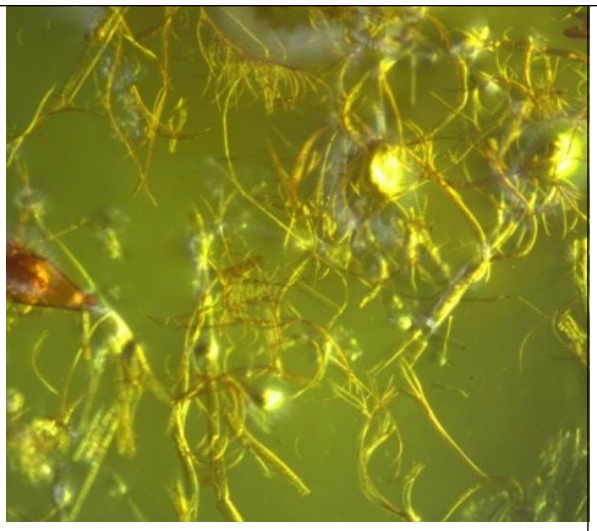


Fig S7. Packing of molecules of **2**, showing formation of dimers with the utilization of weak O-H…H hydrogen bonds (shown in aqua blue color). A view of π···π stacking and *end-to-face* arrangement of molecules.

Table S2. A table showing the photographs of the crystals obtained from crystallizing the solutions of pab at various time of UV exposure using LUZCHEM 4V UV reactor (wavelength 350 nm) with 8 W power, estimated percentage of the bent crystals and percentage of *cis*-pab in the bent crystals as determined from the ^{1}H-NMR spectroscopy analysis.

Time of irradiation	Microscopic images of bulk sample obtained after complete evaporation	estimated percentage of the bent crystals	percentage of *cis*-pab in the bent crystals as determined from the ^{1}H-NMR spectroscopy analysis
T= 0		0%	0%

5 min		5-10%	1.81% ± 0.43
15 min		15-20 %	1.89% ± 0.46
30 min		30-50 %	2.02 % ± 0.43

1 h		80-90 %	2.11 % ± 0.32

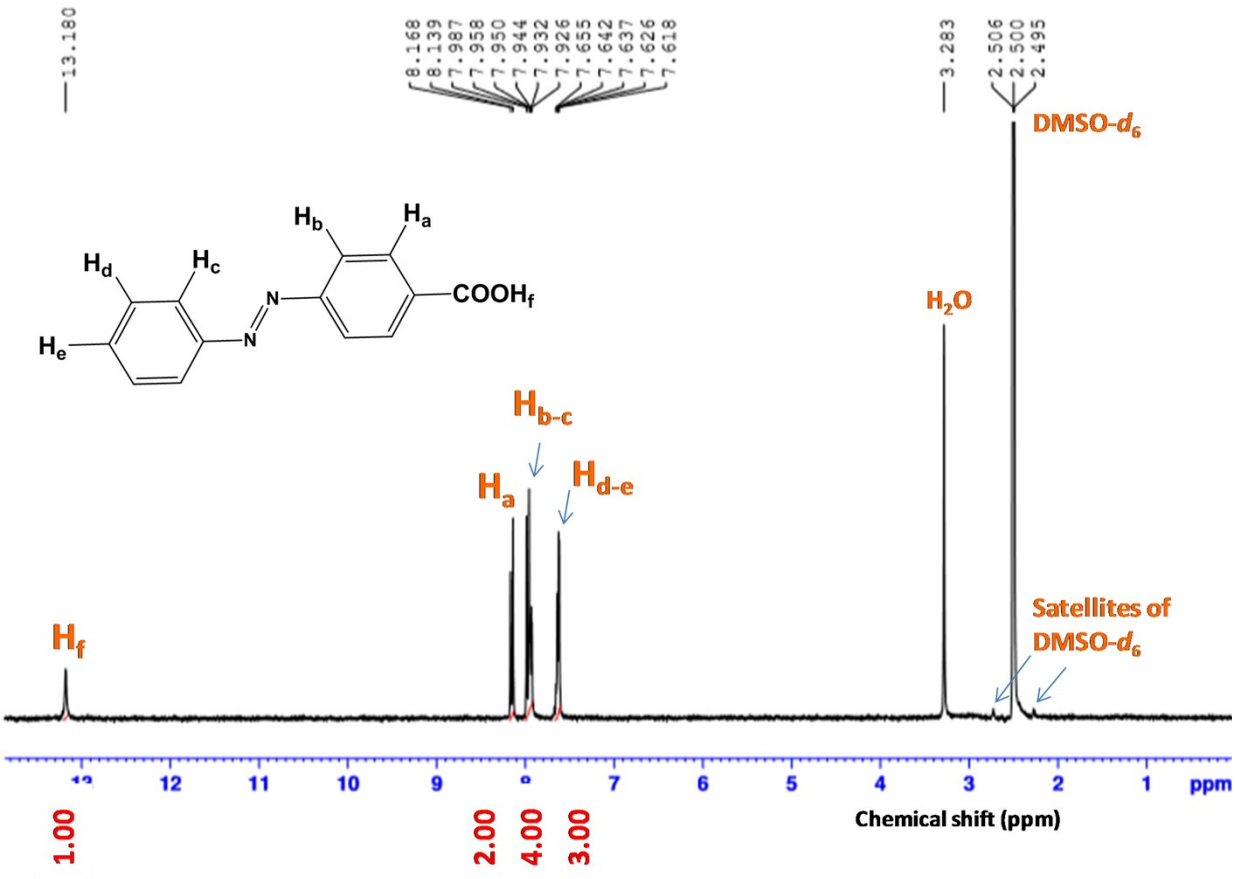


Fig S8. ^{1}H NMR spectrum of straight crystals of pab, **1** in DMSO-d_6.

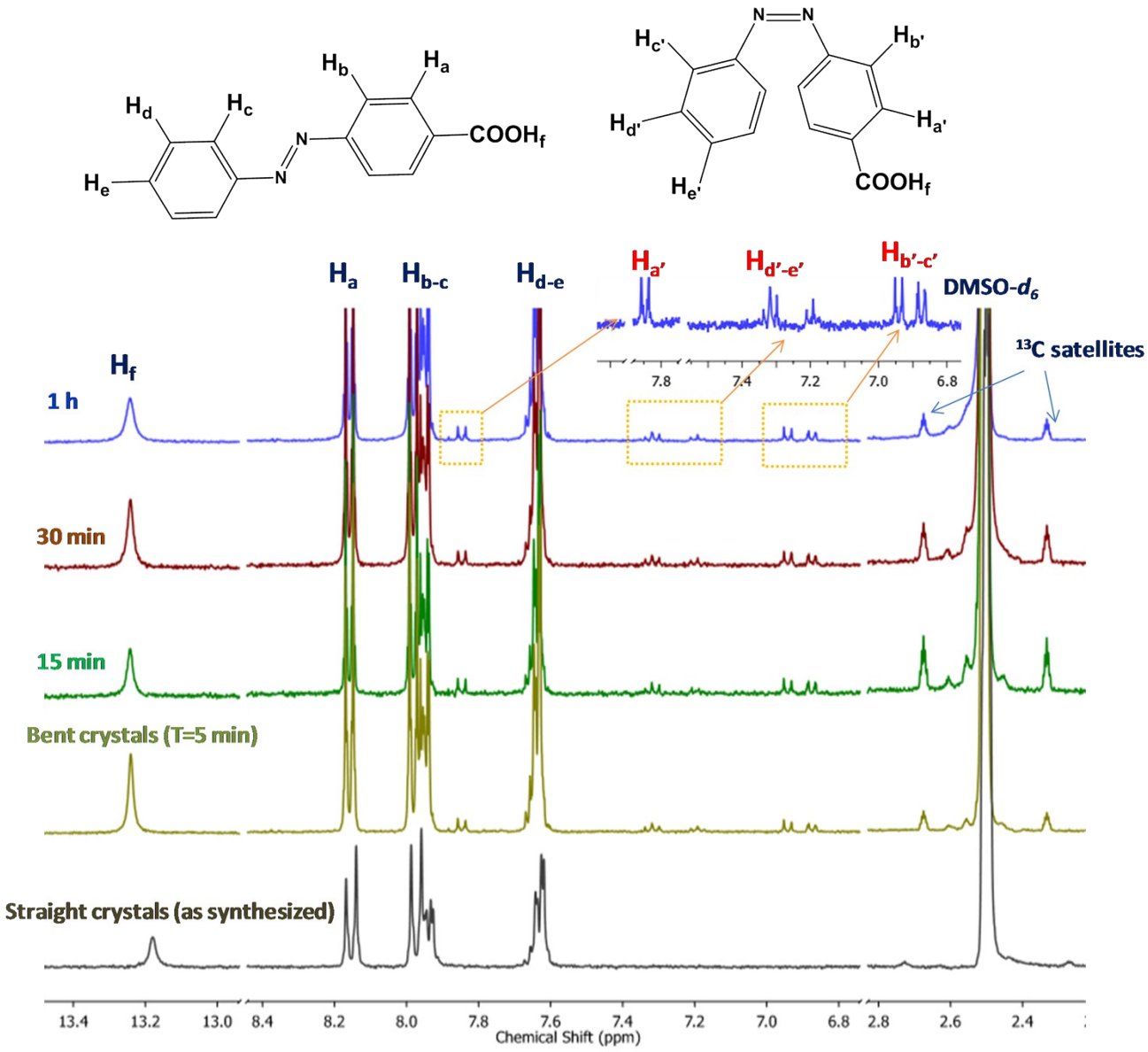
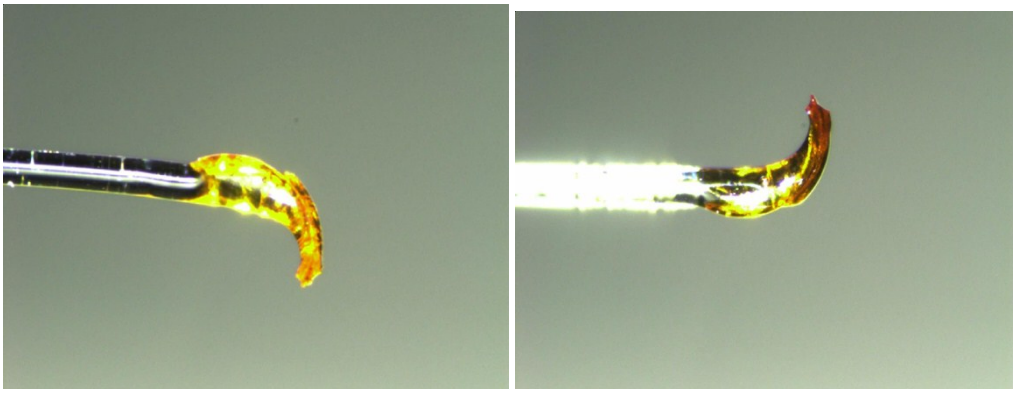


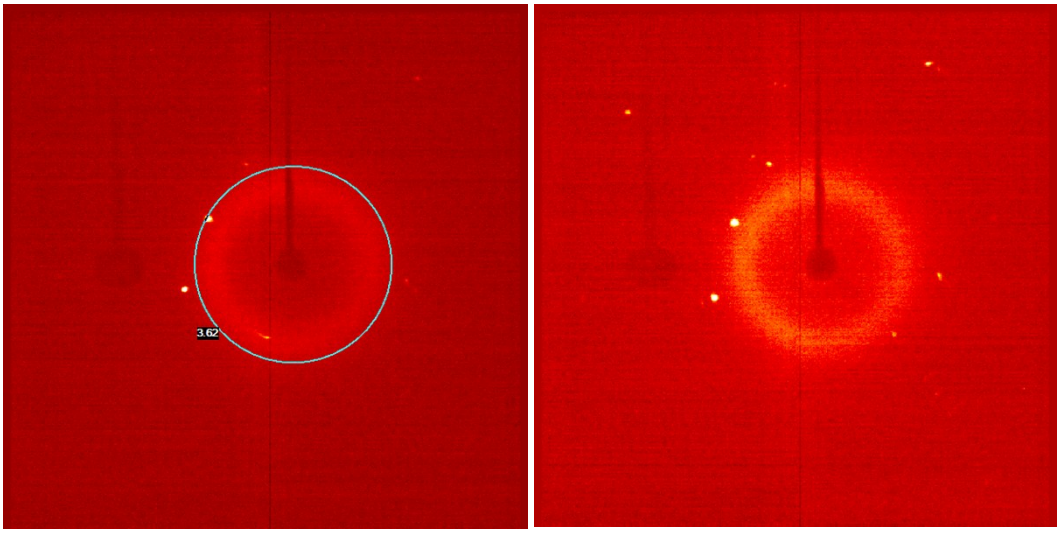
Fig S9. ^{1}H-NMR spectra of bent crystals, **3** obtained at different intervals of time or UV irradiation. The bent crystals were carefully separated from the mixture obtained after complete evaporation of the solutions irradiated with UV light at various intervals and dissolved in DMSO-d_6.

SXRD measurements on bent crystals, 3



a) b)

Fig S10. A bent crystal mounted for measurement at (a) 100K and (b) 298K.



(a) (b)

Figure S11. Diffraction frames of bent crystals (a) 298K (b) 100K. The diffraction spots could not be indexed.

PXRD analyses

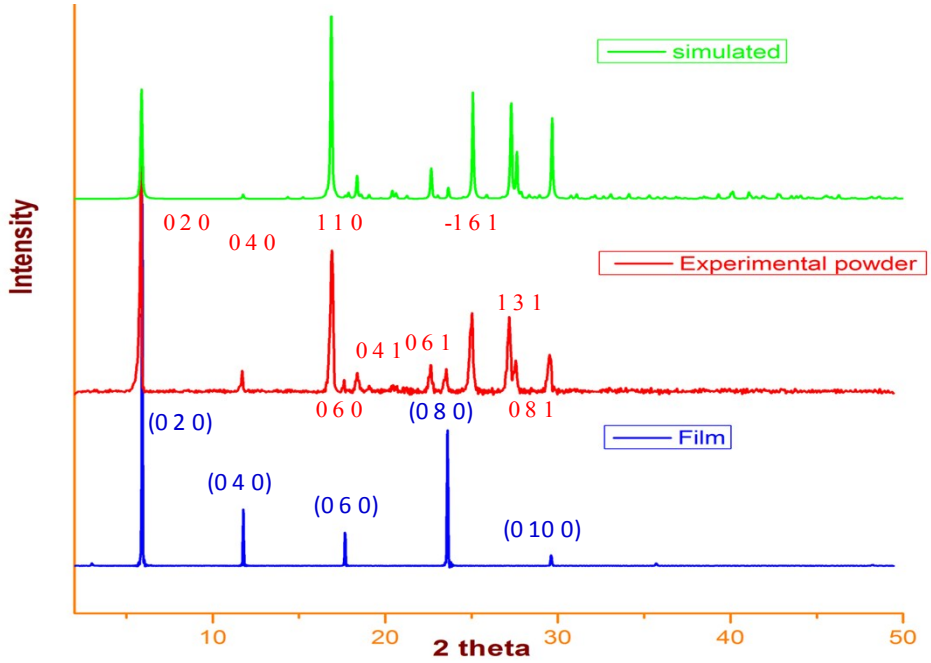


Fig S12. An overlay of PXRD patterns of simulated from the single crystal data, powder and as prepared thin films of pab.

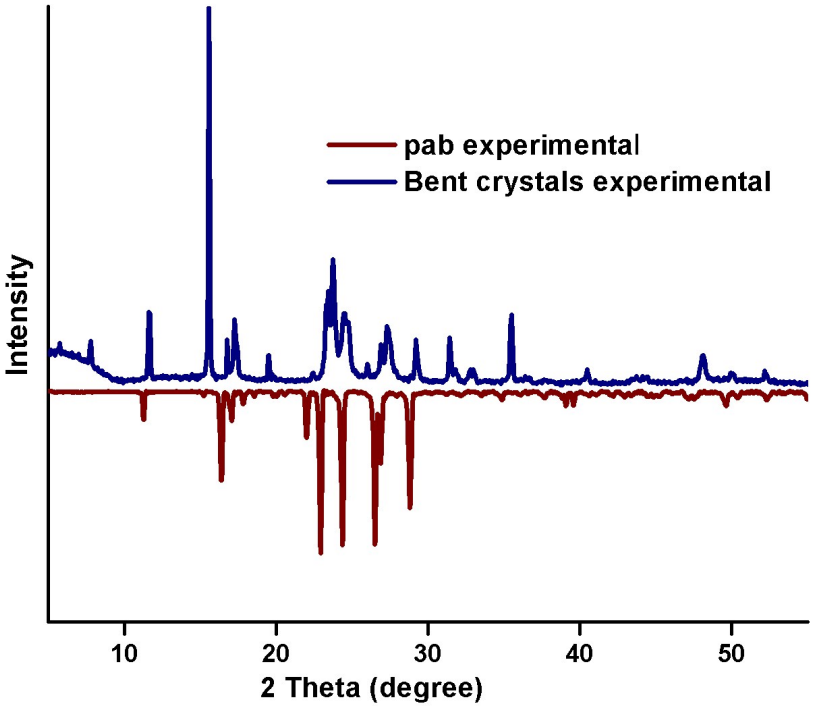


Fig S13. A comparison of experimental PXRD patterns of bent crystals (blue) and normal crystals of pab (maroon).

Thermogravimetric analyses (TGA)

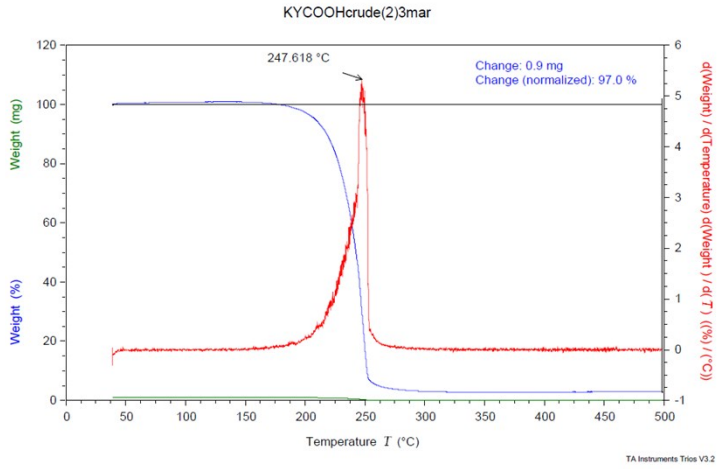


Fig S14. TGA of crystalline powder as synthesized pab, **1.**

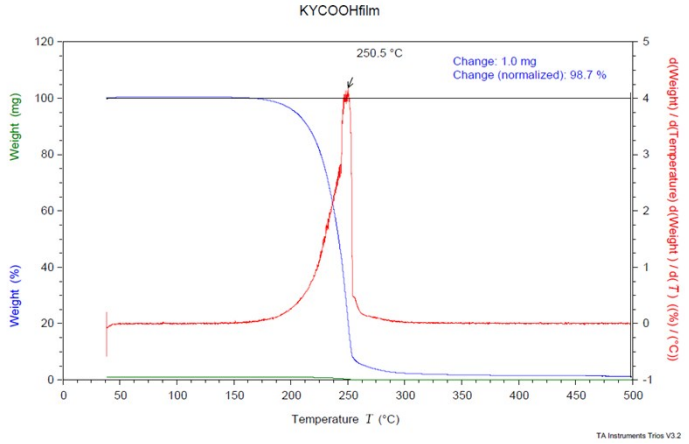


Fig S15. TGA of thin films of pab, **2**

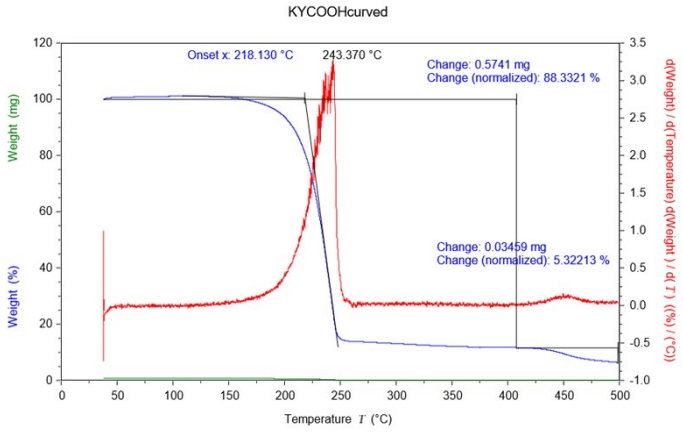


Fig S16. TGA of bent crystals of pab, **3**

References: 1. H. D. Ampson. P-PHENYLAZOBENZOIC ACID. *Org. Synth.* **1945**, *25,* 86.