Supporting information

Photoinduced irreversible transformation from elastic to bent brittle crystals: Importance of reaction pathway in the irreversibility of the molecular movement

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1. Infrared (IR) spectra analysis

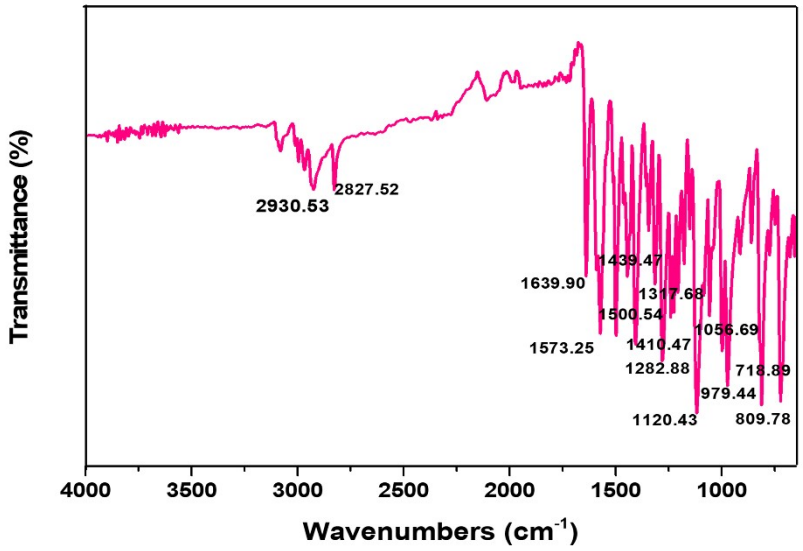


Fig. S1 IR spectra of **TTMP**

Table S1. Functional groups assignment of **TTMP**

Frequency (cm^{-1})	Assignment
2930.53	C-H Stretching
2827.52	C-H Stretching
1639.90	C=O Stretching
1573.25	C=C Aromatic stretching
1500.54	C=C Aromatic Stretching
1439.47	C=C Stretching
1410.47	C-H Deformation
1317.68	C-C Aromatic stretching
1282.88	C-H Bending
1233.93	C-H Bending
1120.43	O-CH_3 Stretching
1056.69	C-O Stretching
809.78	C-S Bending

2. Glide plane and two-fold screw axis of symmetry

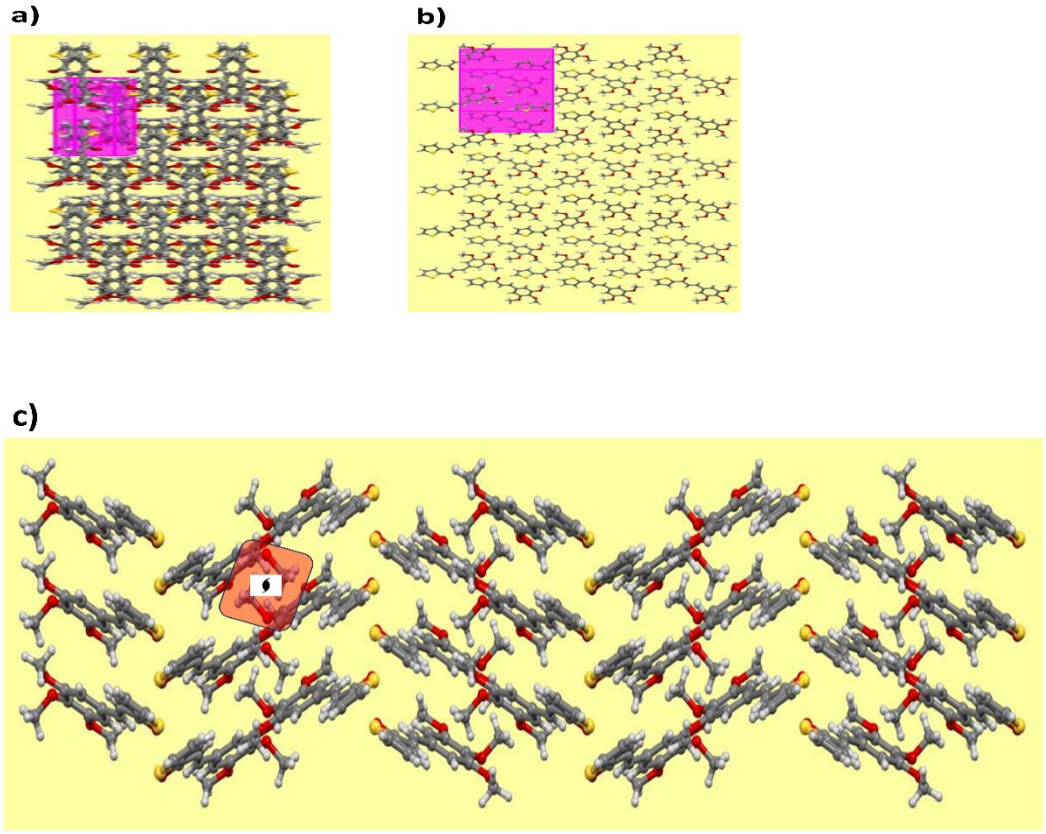


Fig. S2 Glide plane down a) *a* crystallographic axis b) *b* crystallographic axis c) two-fold screw axis along *c* crystallographic axis

3. Proton nuclear magnetic resonance analysis

Table S2. Proton assignment of TTMP before and after sunlight exposure

Different types of protons	Chemical shift in ppm (Before sunlight exposure)	Chemical shift ppm (After sunlight exposure)
Aromatic proton	8.27	8.28
Olefinic proton	8.15	
Aromatic proton	8.07	8.04
Aromatic proton	7.70	7.88
Olefinic proton	7.66	
Aromatic proton	7.58	7.54
$CDCl_3$	7.24	7.24
Methoxy proton	4.32	4.94,4.79,4.71
Cyclobutane proton		5.57
Cyclobutane proton		5.46

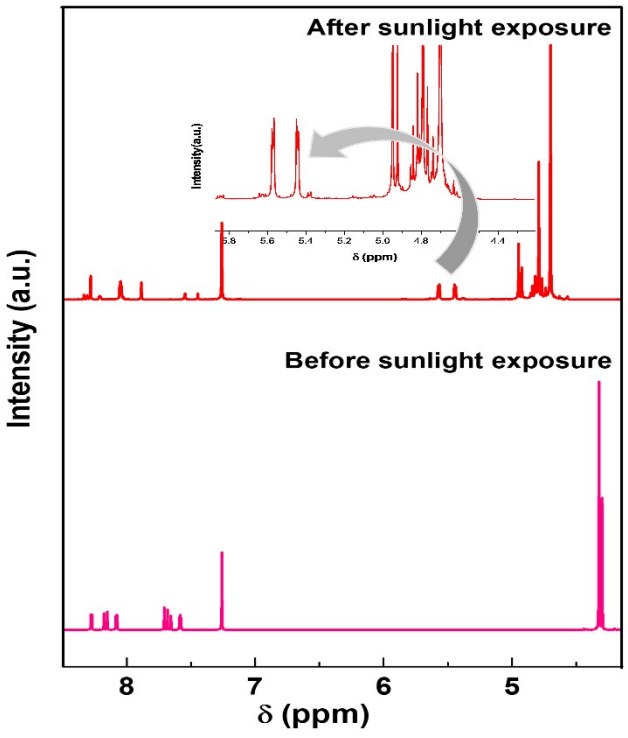


Fig. S3 ^{1}H-NMR spectra of TTMP before and after sunlight exposure

4. Carbon nuclear magnetic resonance analysis

Table S3. Carbon assignment of TTMP before and after sunlight exposure

Different types of Carbon atoms	Chemical shift in ppm (Before sunlight exposure)	Chemical shift ppm (After sunlight exposure)
Carbonyl carbon	182.94	190.00
Aromatic carbon	153.56	153.03
Aromatic carbon	145.60	145.21
Aromatic carbon	144.44	143.08
Aromatic carbon	140.99	137.12
Aromatic carbon	133.99	133.72
Aromatic carbon	131.92	131.92
Olefinic carbon	130.36	
Aromatic carbon	128.27	128.09
Olefinic carbon	120.95	
Aromatic carbon	105.40	105.55
$CDCl_3$	77	77
Methoxy carbon	60.75	61.10
Methoxy carbon	66.14	56.40
Cyclobutane carbon		45.83
Cyclobutane carbon		45.14

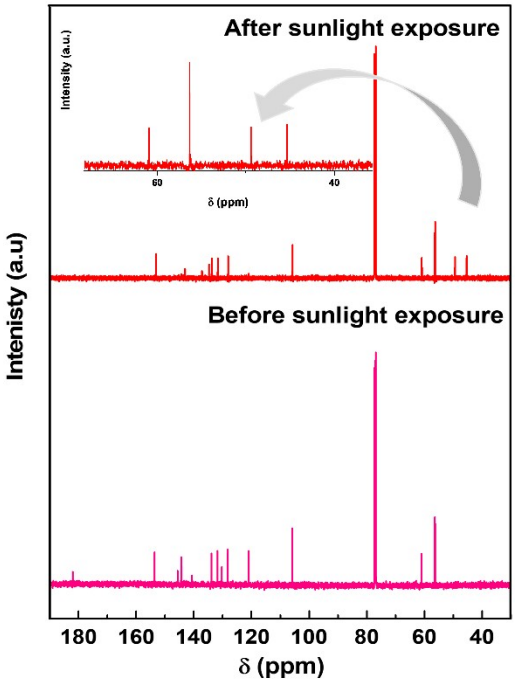


Fig. S4 ^{13}C-NMR spectra of TTMP before and after sunlight exposure

5. Differential scanning calorimetry (DSC) analysis

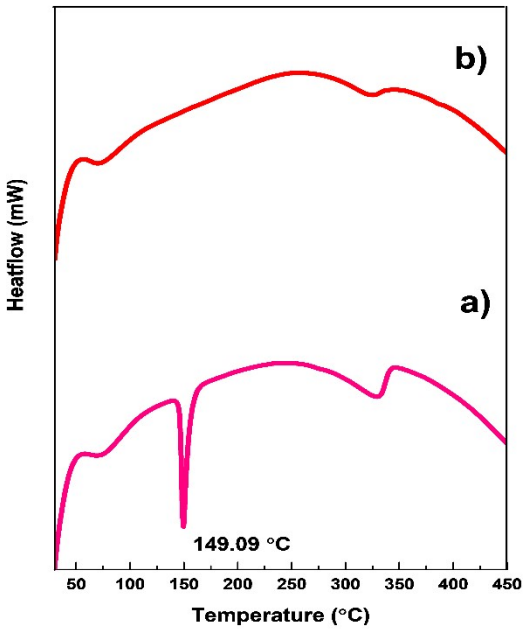
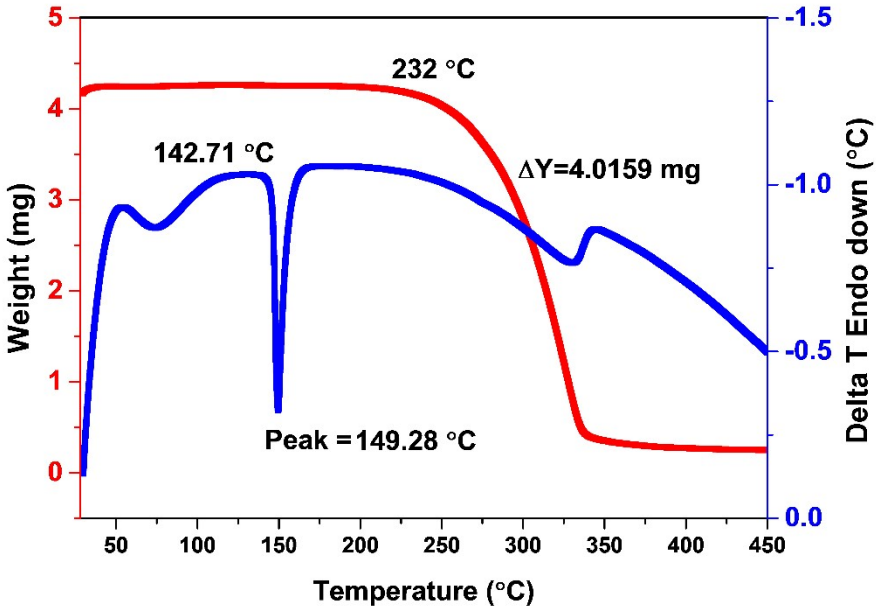


Fig. S5 DSC curves of TTMP a) before and b) after sunlight exposure

6. Thermogravimetric (TG) and differential thermal analysis (DTA)

a)



b)

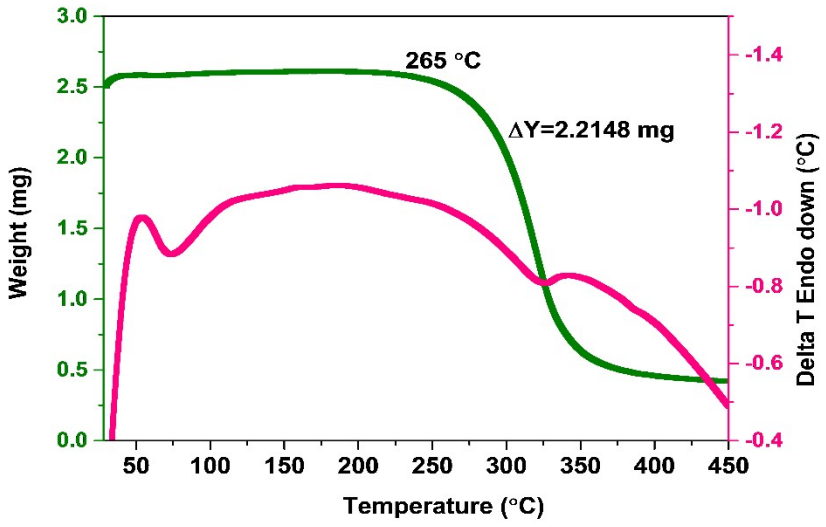


Fig. S6 Thermogravimetric and differential thermal analysis of TTMP a) before and b) after exposure

7. Parallel orientation of chalcone molecules

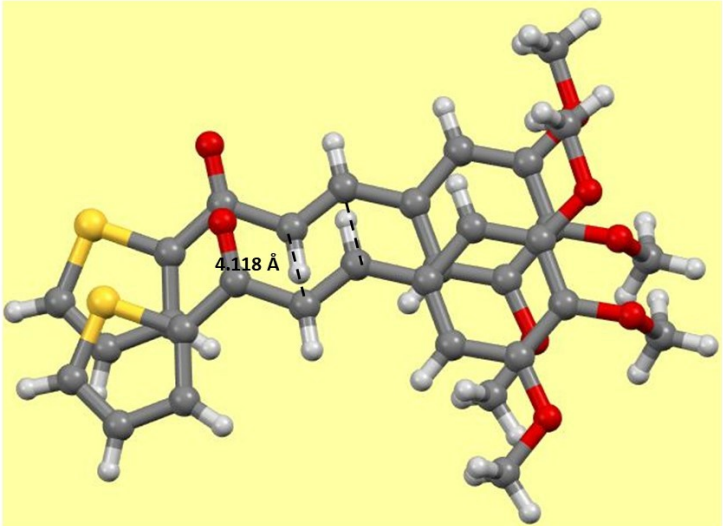


Fig. S7 Distance between two parallelly oriented TTMP molecules

8. List of Photoinduced bending molecules through [2+2] dimerization

Table S4. List of reported photoinduced bending molecules through [2+2] dimerization

Compound name with reference no.	CCDC NO.	Elastically bending	Reversible/irreversible with respect to light/heat	Bond distance (Å)	Time taken for bending	Crystallinity of product
Barbiturate derivative[32]	2258875	Yes	Not analyzed	5.615	48 hours	Crystalline
5- chloro-2-(naphthalenylvinyl)benzo [d]oxazole[28]	1904295	No	Reversible	3.83	5 minutes	Crystalline
1,2-Bis(4-pyridyl)ethylene- Based Pyridinium Salt[15b]	923356	No	Reversible	3.6	48 hours	Crystalline
7-Methoxycoumarin[15c]	2061357	No	Reversible	3.83	24 hours	Crystalline

1-(4-bromophenyl)-3-(4-fluorophenyl)-prop-2-en-1-one[19]	1974692	No	Reversible	4.01	60 minutes	Crystalline
(E)-3-(3,5-difluorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one[19]	1974670	No	Reversible	3.936	60 minutes	Crystalline
(E)-2-(2,4-dichlorostyryl)benzo[d]oxazole[21]	1526199	No	Reversible	3.86	5 minutes	Crystalline
cyanostilbene esters[29]	1983911	No	Not analyzed	4.687	10 minutes	Crystalline
(E)-2-(4-fluorostyryl)benzo[d]oxazole[30]	1814882	No	Reversible	3.681	10 minutes	Crystalline
(E)-2-(2,4-difluorostyryl)benzo[d]oxazole[30]	1814128	No	Reversible	3.863	10 minutes	Crystalline
(E)-2-(4-fluorostyryl)benzo [d]thiazole[31]	1814131	No	Reversible	3.829	4 minutes	Crystalline
(E)-2-(2,4-difluorostyryl) benzo[d]thiazole[31]	1814889	No	Reversible	3.822	4 minutes	Crystalline
(*Z*)-2-(3,5-bis(trifluoromethyl)phenyl)-3-(naphthalen-2-yl) acrylonitrile[7]	2032920	Yes	Reversible	3.607	30 minutes	Crystalline
1,3-dimethylbarbituric acid [33]	2332071	No	Reversible	3.621	12 hours	Crystalline
(E)-4-fluoro-cinnamaldehyde malononitrile[27]	1973164	No	Irreversible	3.376	Not specified	Amorphous

9. List of Videos

Video S1- Mechanical bending of TTMP Crystal before sunlight exposure

Video S2- Breaking of TTMP crystal after sunlight exposure on the application of mechanical force