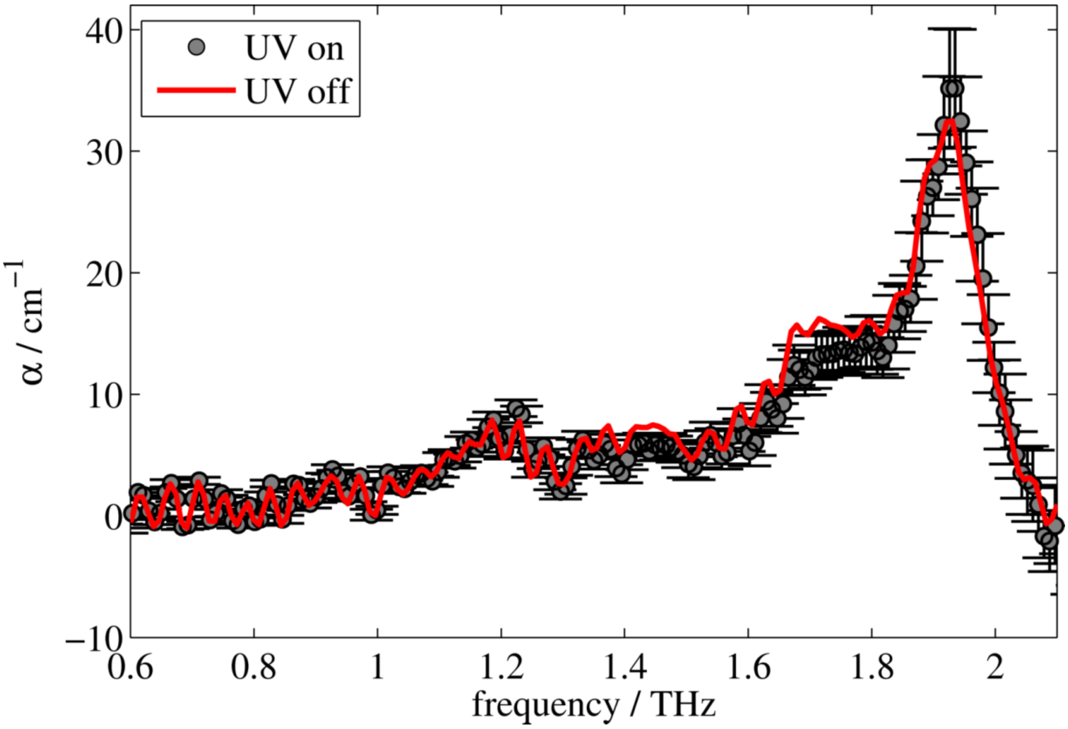
Supplementary information

UV illumination test



Supplementary Figure 1: Terahertz spectra of the TPE compound before UV illumination (red solid line) and with UV (grey circles) at low temperatures. The data agree to within the experimental accuracy of the measurement.

As is shown in Supplementary Figure 1, no change was observed in the terahertz spectra before UV illumination and during UV illumination, indicating that there are no isomerisation reactions being caused by the UV excitation.

Crystal structures and vibrational mode assignment

Supplementary Table 1 records the equilibrium torsion angles for the 8 phenyl moieties in the high and low temperature unit cell, as well as the change.

Supplementary Table 1 Torsion angles for the 8 phenyl moieties at both high and low temperatures.

Phenyl type[a]	High Temperature	Low Temperature	change
1	136.03	137.82	1.79
1*	-45.74	-44.63	1.11
2	-55.83	-56.43	-0.60
2*	125.42	123.72	-1.70
3	-48.33	-45.53	2.80
3*	134.32	138.32	4.00
4	134.62	132.72	-1.90
4*	-46.13	-48.23	-2.10

[a] Following the nomenclature of Fig. 2(c). The * indicates the two molecules. All measurements are given in degrees.

Supplementary Table 2 details the structure parameters of the calculated crystal structures (generated from single-crystal x-ray diffraction data (XRD)) at high (293 K) and low (110 K) temperatures. The new crystal structure parameters after geometry optimization in CASTEP are also shown, along with the percentage change (where applicable). The structure files determined from the XRD measurements are also provided. No solvent molecules were present in the XRD materials or in the powdered samples used in the terahertz measurements.

Supplementary Table 2 Crystal structure parameters for the high and low temperature structures as determined from XRPD and after geometry optimization in CASTEP.

	High Temperature			Low Temperature		
Parameter	XRPD	CASTEP	% change	XRPD	CASTEP	% change
Space Group	P 2_1	P 2_1	-	P 2_1	P 2_1	-
a / Å	9.8371	9.6608	-1.79	9.7772	9.6617	-1.18
b / Å	9.5018	8.7061	-8.37	9.1723	8.7121	-5.02
c / Å	10.7088	10.8045	0.89	10.7781	10.7976	0.18
α / deg.	90.00	90.00	0.00	90.00	90.00	0.00
β / deg.	107.166	108.054	0.83	108.052	108.070	0.02
γ / deg.	90.00	90.00	0.00	90.00	90.00	0.00
volume / Å^3	956.341	864.003	-9.66	918.967	864.053	-5.98

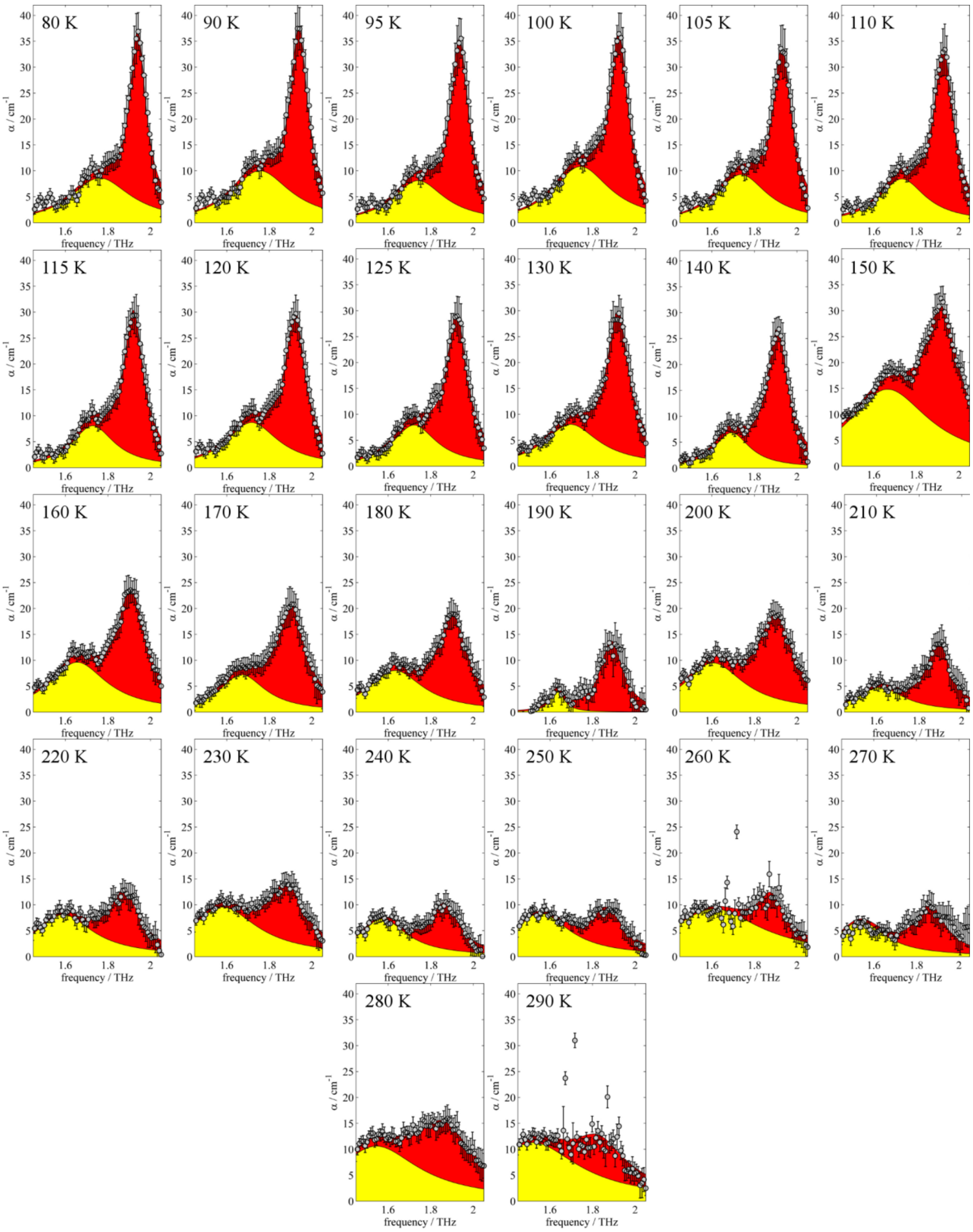
As explained in the main body of the text, the CASTEP calculations were performed using the semi-empirical dispersion correction module, thereby incorporating London type dispersion forces. Initially, the unit cell dimensions were allowed to change for both temperatures, but as explained in the main text both high and low temperature structures optimized to the same geometry, and the observed differences in structure were lost. In an attempt to preserve some of the high temperature character, the unit cell dimensions were fixed for the high temperature geometry optimization. So as to incorporate London dispersion forces in the calculation of the vibrational modes, the finite displacement method was implemented. The predicted vibrational frequencies and their descriptions are shown in Supplementary Table 3.

Supplementary Table 3 Predicted vibrational frequencies and intensities for the high and low temperature TPE structures.

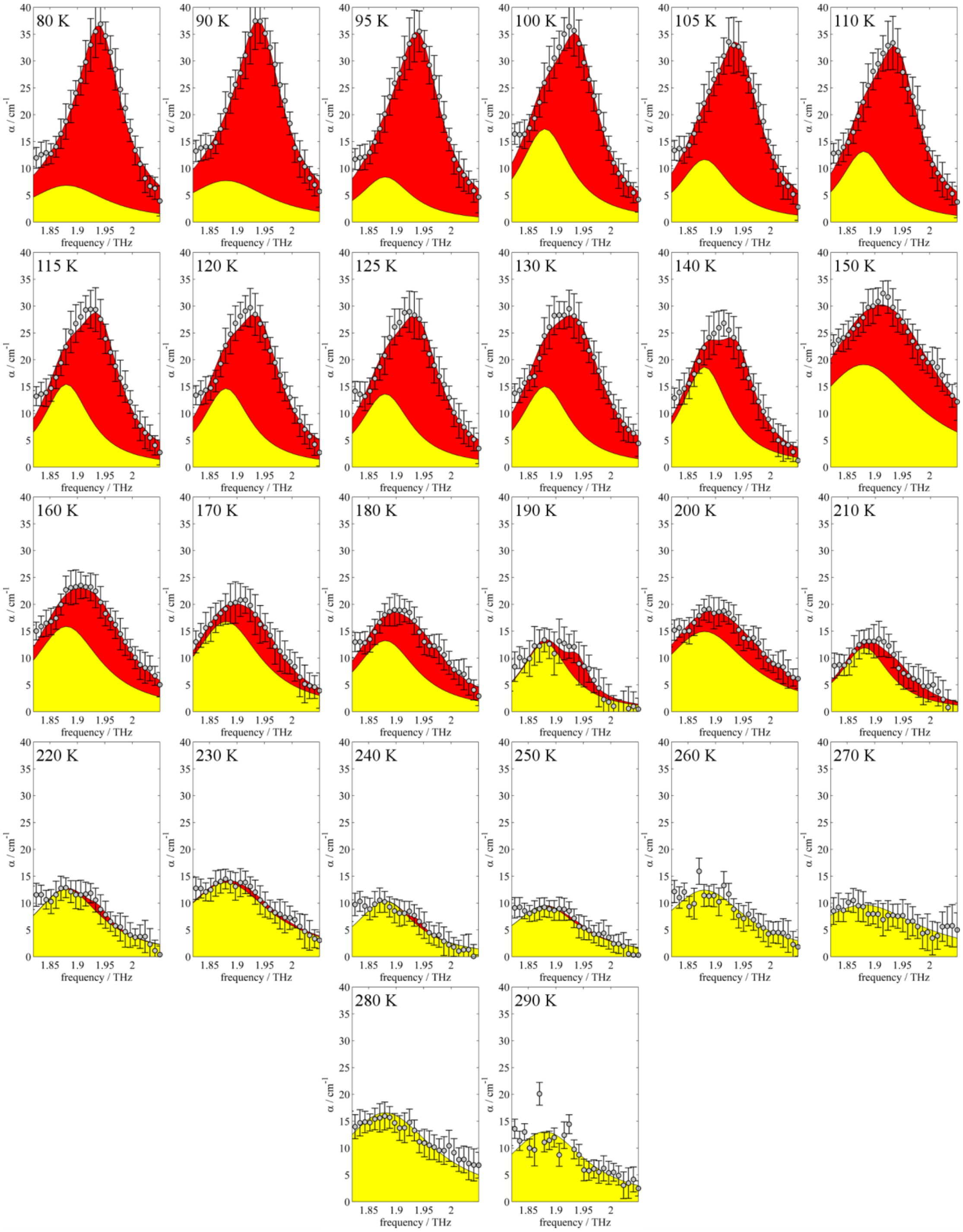
Frequency / THz	Frequency / cm^{-1}	Intensity / a.u.	Description[a]
			High temperature structure
0.73	**24.33**	**0.01044**	**ph1 large twist**; ph3 out of plane rock
0.78	25.94	0.00146	**ph1 in plane rock**; ph2 small out of plane rock; ph3 small out of plane rock, twist; ph4 small twist
0.98	32.78	0.00236	ph1 out of plane rock; ph2 in plane rock; ph3 twist; **ph4 in plane rock**
1.07	**35.66**	**0.02151**	ph1 small twist; ph2 small in plane rock; ph3 in plane rock; **ph4 out of plane rock**
1.26	**42.15**	**0.00658**	**ph1 in plane rock**; **ph2 in plane rock**; ph3 out of plane rock, small twist; ph4 small out of plane rock
1.49	**49.74**	**0.00779**	**ph1 in plane rock, twist**; **ph2 in plane rock**; ph3 twist; ph4 in plane rock
1.51	**50.35**	**0.00609**	**ph1 in plane rock, small twist**; **ph2 in plane rock**; ph3 small twist; ph4 in plane rock, small twist
1.53	51.19	0.00147	**ph1 twist, small out of plane rock**; ph2 in plane rock; ph3 small twist; ph4 small in plane rock
1.60	**53.37**	**0.01822**	ph1 in plane rock, small twist; ph2 small twist; ph3 out of plane rock, small twist; **ph4 in plane rock, twist**
1.66	**55.54**	**0.03203**	ph1 small twist; ph2 small twist; ph3 out of plane rock, twist; **ph4 in plane rock, twist**
1.74	57.93	0.00261	**ph1 twist, out of plane rock**; ph2 in plane rock, small twist; ph3 twist, out of plane rock; ph4 out of plane rock
1.94	64.81	0.00034	Insignificant
2.09	69.79	0.00123	**ph1 large out of plane rock**; ph2 twist; ph3 small twist; ph4 in plane rock, small twist
2.12	**70.83**	**0.00669**	**ph1 twist**; **ph2 twist**, small in plane rock; ph3 small in plane rock; ph4 small twist
2.31	77.22	0.00055	Insignificant
2.41	80.30	0.00178	ph1 twist, out of plane rock; ph2 small twist; **ph3 out of plane rock, twist**; ph4 out of plane rock
2.46	**82.07**	**0.00768**	ph1 small twist; ph2 in plane rock, twist; **ph3 twist, small in plane rock**; **ph4 twist**
			Low temperature structure
0.84	27.95	0.00011	Insignificant
0.99	33.01	0.00003	Insignificant
1.43	**47.66**	**0.01162**	ph1 in plane rock, small twist; ph2 in plane rock; ph3 twist; **ph4 in plane rock, small twist**
1.50	**50.02**	**0.01106**	**ph1 large in plane rock, twist**; ph2 twist; ph3 small out of plane rock, twist; ph4 out of plane rock
1.81	60.54	0.00002	Insignificant
1.91	**63.55**	**0.00564**	ph1 out of plane rock; **ph2 in plane rock, twist**; **ph3 in plane rock, twist**; ph4 twist
1.94	**64.71**	**0.00116**	**ph1 out of plane rock**; ph2 twist; **ph3 twist**; ph4 twist
2.01	**66.95**	**0.00438**	**ph1 in plane rock**; **ph2 twist, out of plane rock**; ph3 in plane rock, small twist; ph4 small out of plane rock
2.13	**70.98**	**0.08590**	ph1 small twist; **ph2 large in plane rock, small twist**; ph3 twist, small in plane rock; **ph4 out of plane rock, small twist**
2.14	**71.24**	**0.00406**	**ph1 twist**; ph2 out of plane rock; ph3 out of plane rock, twist; ph4 small twist
2.40	**79.98**	**0.02293**	ph1 in plane rock; **ph2 out of plane rock, twist**; **ph3 in plane rock, small twist;** ph4 out of plane rock
2.41	**80.40**	**0.00576**	**ph1 in plane rock, twist**; **ph2 in plane rock, twist**; **ph3 in plane rock**; ph4 small out of plane rock

[a] Descriptions of the motions are given for the vibrational modes following the nomenclature defined in Fig. 2(c). The description has the following key for each vibration: **bold** indicates dominant motions, underline indicates other significant motions and undecorated font indicates the minor motions.

Fitting results



Supplementary Figure 2: Fits for frequency range between 1.45 and 2.05 THz for all data between 80 K and 290 K. The two shaded regions correspond to the contribution of each harmonic oscillator towards the resulting terahertz spectrum.



Supplementary Figure 3: Fits for frequency range between 1.82 and 2.05 THz (i.e. modeling the large spectral feature) for all data between 80 K and 290 K. The two shaded regions correspond to the contribution of each harmonic oscillator towards the resulting terahertz spectrum.