Supplementary Material (ESI) for Chemical Communications
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Supplementary Material for *Chemical Communications*

Reversible Single-Crystal to Single-Crystal Polymorphic Phase Transformation of an Organic Crystal

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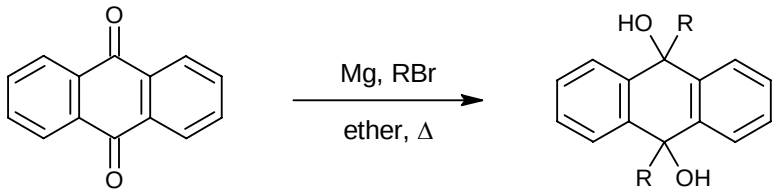
Electronic Supplementary Information (ESI)

(12 pages)

Synthesis of I



R = *p*-MeO-C_6H_4

The synthesis was, as far as possible, carried out under inert conditions. A solution of *p*-bromoanisole (12.66 ml, 100 mmol) in dry diethyl ether (30 ml) was prepared. An initial volume of 5 ml of this solution was added to a gently refluxing, stirred mixture of magnesium (2.4 g, 98.7 mmol) in dry diethyl ether (20 ml). When the reaction had begun, the remainder of the *p*-bromoanisole-solution was added dropwise over a period of approximately 30 minutes. The reacting mixture was allowed to reflux for 2 h. The resulting Grignard reagent was added to a vigorously stirring, gently refluxing suspension of anthraquinone (4.0 g, 19.2 mmol) in dry diethyl ether (120 ml). The reaction was allowed to continue under reflux for 15-20 h. The resulting mixture was cooled on ice and acidified to a pH of 2 using hydrochloric acid (2.5 M). A grey-green precipitate resulted and was added to boiling acetone (500 ml). The mixture was filtered hot after heating for at least a further 10 minutes. The residue was discarded and the filtrate reduced to approximately 100 ml using a rotary evaporator. Cooling on ice allowed the reaction product to precipitate. Purification was done by recrystallization from acetone and thereafter, washing thoroughly with a minimum amount (approximately 40 ml) of warm benzene. The compound was characterized by NMR spectroscopy, FTIR spectroscopy (hydroxy peak at 3563 cm^{-1}) and SCD analysis.

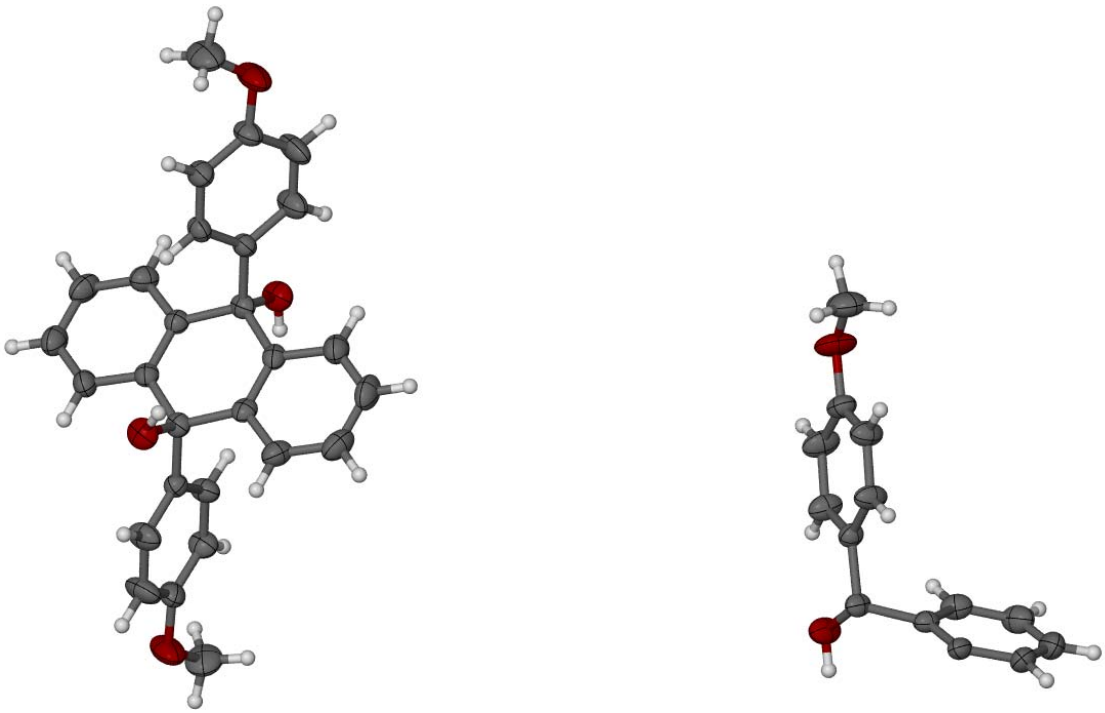
NMR data: ^{1}H (400 MHz, $CHCl_3$-*d*) δ 1.55 (s, 3 H), δ 2.59 (s, 2 H), δ 3.78 (s, 6 H), δ 6.82 (d, *J*=8.95 Hz, 4 H), δ 7.15 - 7.29 (m, 4 H), δ 7.35 (d, *J*=9.83 Hz, 8 H).

^{13}C (100MHz, $CHCl_3$-*d*): δ55.20, δ74.20, δ113.31, δ127.82, δ128.18, δ128.30, δ140.16, δ140.93, δ158.31.

Single-crystal X-ray diffraction:

Crystals of **Ia** and **Ib** were prepared by slow evaporation of benzene and dichloromethane solutions of compound **I**, respectively. **Ia** was also prepared by crystallization from nitrobenzene or toluene solutions of **I** and **Ib** was also prepared from chloroform and dichloroethane solutions of **I**. Single crystal X-ray data of those crystals were collected at 21 °C on Bruker SMART Apex diffractometer equipped with a CCD area detector.

Variable temperature single-crystal experiments were performed on a crystal which was glued to a thin glass fiber and enveloped in a temperature-controlled stream of dry nitrogen gas during intensity data collection. The temperature of the crystal was controlled using an Oxford Cryosystream Plus cryostat. The unit cell was determined at 0 °C. The single-crystal data were recorded at -50 °C and then the crystal was heated to 50 °C and the intensity data were measured. Crystallographic details of the variable temperature experiment are given in Table 2.



a **b**

Fig. 1 Thermal ellipsoid plots of the asymmetric units of (a**) Ia** and (b) **Ib**. Ellipsoids are shown at the 50% probability level.

Hirshfeld surfaces of Ia and Ib:

a **b**

Fig. 2 Hirshfeld surfaces of (a) **Ia** and (b) **Ib**.

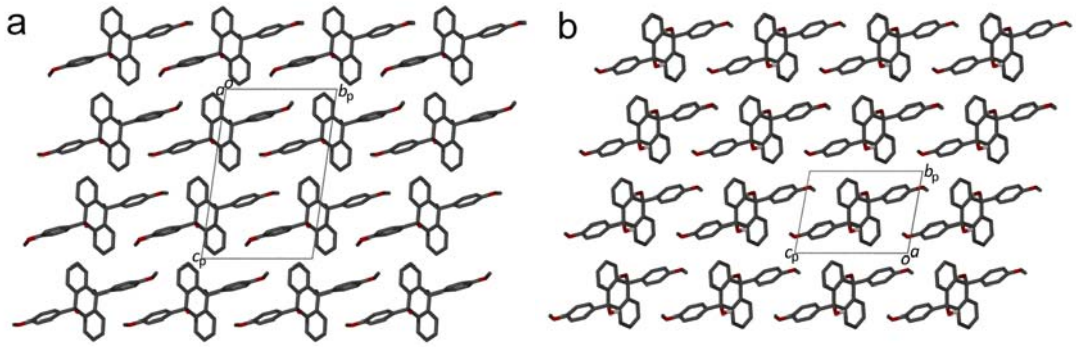


Fig. 3 Packing diagrams of (a) **Ia**, viewed along [100] and (b) **Ib**, viewed along [-100]. Hydrogen atoms are omitted for clarity.

FTIR of **I**:

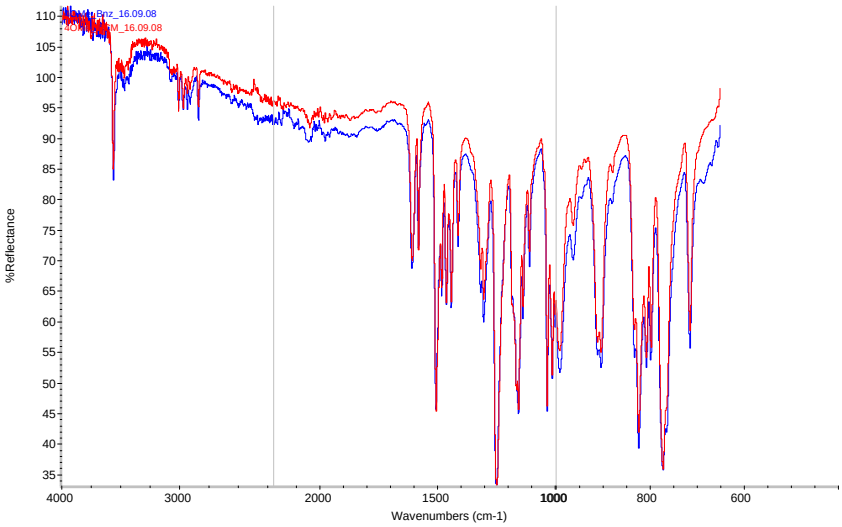


Fig. 4. FTIR spectrum showing the conversion of **Ib** to **Ia** upon crushing.

Table 1. Hydrogen bonding geometry in **Ia** and **Ib**[*]

	D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	∠D–H…A (°)
	O(2)–H(2)…O(1)	0.98	2.21	2.994(3)	136
Ia	C(7)–H(7)…O(3)	1.08	2.48	3.270(3)	129
	C(12)–H(12)…O(4)	1.08	2.50	3.328(3)	132
Ib	C(4)–H(4)…O(2)	1.08	2.62	3.631(4)	155
	C(7)–H(7)…O(1)	1.08	2.72	3.669(4)	146

[*]All hydrogen atoms were placed in calculated positions with C-H and O-H bond distances neutron-normalized.

Table 2. Crystallographic details

Compound	**Ia**	**Ib**
Formula	$C_{28}H_{24}O_4$	$C_{28}H_{24}O_4$
Formula weight	424.47	424.47
T/K	294	294
Crystal System	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a/Å	6.2160(9)	6.305(3)
b/ Å	10.9301(16)	8.330(4)
c/ Å	16.315(2)	11.095(6)
α/°	97.721(3)	95.273(8)
β/°	90.851(3)	105.204(8)
γ/°	105.319(3)	106.321(8)
V/ Å^3	1057.9(3)	531.0(5)
Z	2	1
D_c/g cm^{-1}	1.333	1.327
μ/mm^{-1}	0.088	0.088
F_{000}	448	224
$2\theta_{max}$/°	56.7	56.7
Total reflections	8480	5410
Unique reflections	4786	2402
Reflections $I > 2\sigma(I)$	2499	1532
Parameters	293	193
R_{int}	0.0335	0.0373
R [F, I > 2σ(I)	0.0663	0.0554
wR (F^2, all data)	0.1441	0.1380
GooF	0.983	1.010

Table 3. Crystallographic details of variable temperature single crystal X-ray diffraction study on same crystal

Temperature of study (K)	273 (initial)	223	323
Crystal System	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a/Å	6.223(2)	6.302(3)	6.194(5)
b/ Å	10.933(3)	8.287(4)	10.864(9)
c/ Å	16.298(5)	11.030(5)	16.293(14)
α/°	97.70(2)	95.460(7)	97.836(14)
β/°	90.89(2)	105.269(7)	90.907(15)
γ/°	105.30(2)	106.343(8)	105.291(14)
V/ Å^3		524.2(4)	1046.2(16)
Z		1	2
D_c/g cm^{-1}		1.345	1.347
μ/mm^{-1}		0.089	0.089
F_{000}		224	448
$2\theta_{max}$/°		49.8	50.3
Total reflections		4911	7393
Unique reflections		1806	3623
Reflections $I > 2\sigma(I)$		1174	1852
Parameters		147	293
R_{int}		0.0607	0.0795
R [F, I > 2σ(I)		0.0739	0.1192
wR (F^2, all data)		0.1534	0.2672
GooF		1.091	1.125

Photographs of crystals recorded during the variable temperature single-crystal X-ray diffraction study:

a **b** **c**

Fig. 5 Photographs of the same crystal were taken at (a) 0 °C, (b) -50 °C and (c) 50 °C during the variable temperature single crystal X-ray diffraction experiment. Although it seems that the crystal degraded at -50 °C and 50 °C, full intensity data were collected and the structures were solved using these data. The mosaicities of the crystal at different temperatures are given bellow.

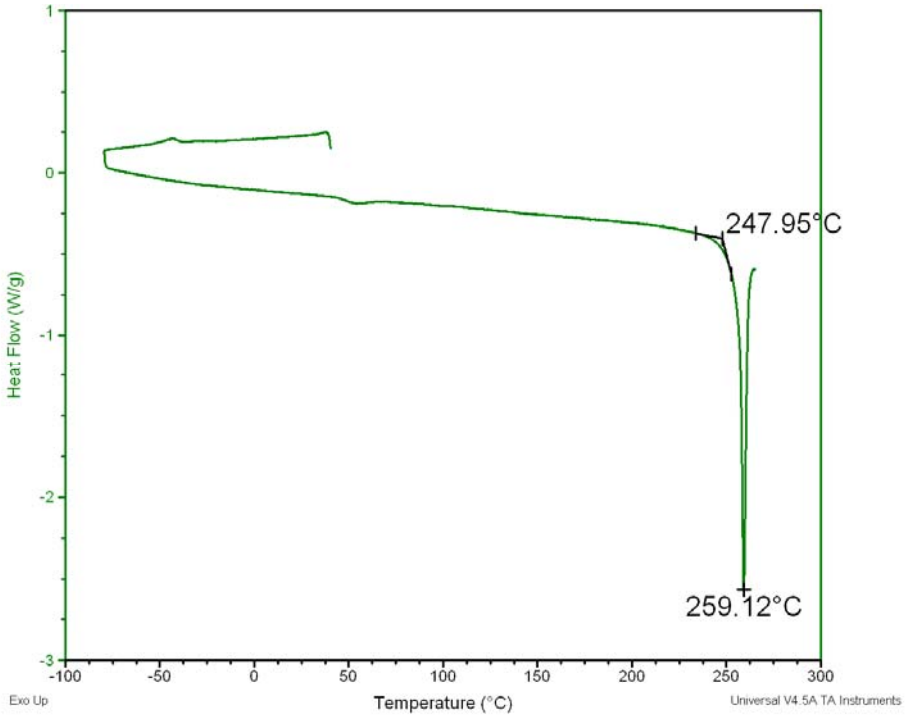
Table 4. Mosaicity of the crystal determined at different temperature:

Temperature (°C)	0 (initial)	-50	0 (final)	50
Mosaicity	0.80	0.93	0.88	0.88

Differential Scanning Calorimetry

Differential scanning calorimetry was carried out on powdered samples using a TA Instruments Q100 calorimeter. Approximately 10 mg of the sample was sealed in a crimped aluminum pan with a hole pierced in the lid. The experiment was carried out under nitrogen purge. At first the sample was cooled to -80 °C at a rate of 10 °C per minute. Then the sample was heated at the same rate until melting occurred.

DSC of **I**



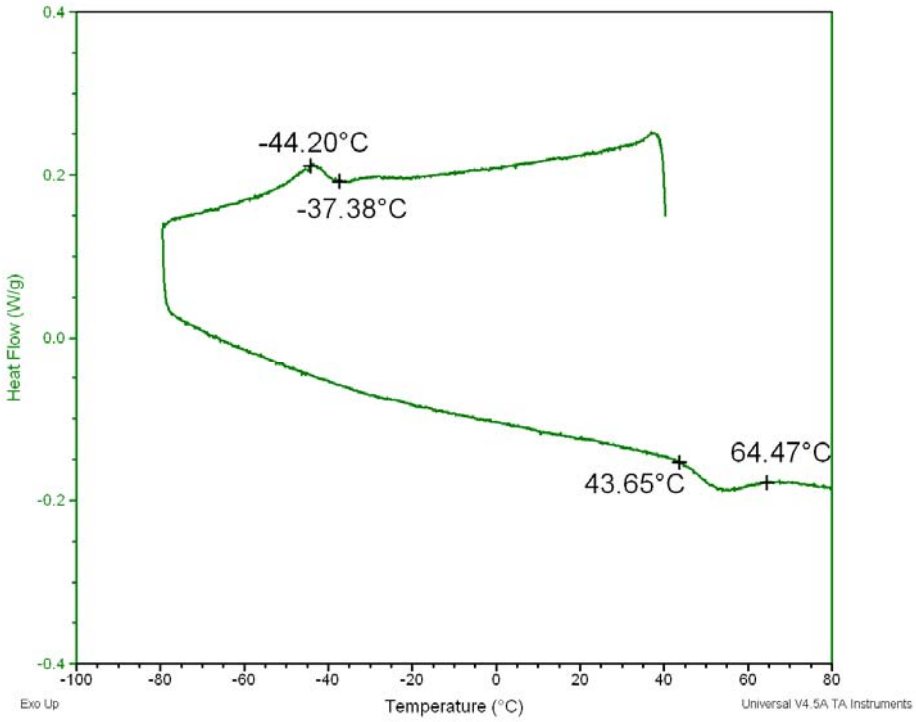


Fig. 6 DSC thermogram of the as-synthesized compound.

Variable temperature powder diffraction study:

Powdered samples were placed on a flat aluminum sample holder. X-ray powder diffractograms were measured using Cu K_α radiation (λ= 1.5418 Å, 45 kV and 40 mA) on a PANalytical instrument operating in Bragg-Brentano geometry. The diffractorgams were measured in the 2θ range 5º to 40º. The temperature of the sample was controlled using an Anton Paar TCU 100 temperature control unit.

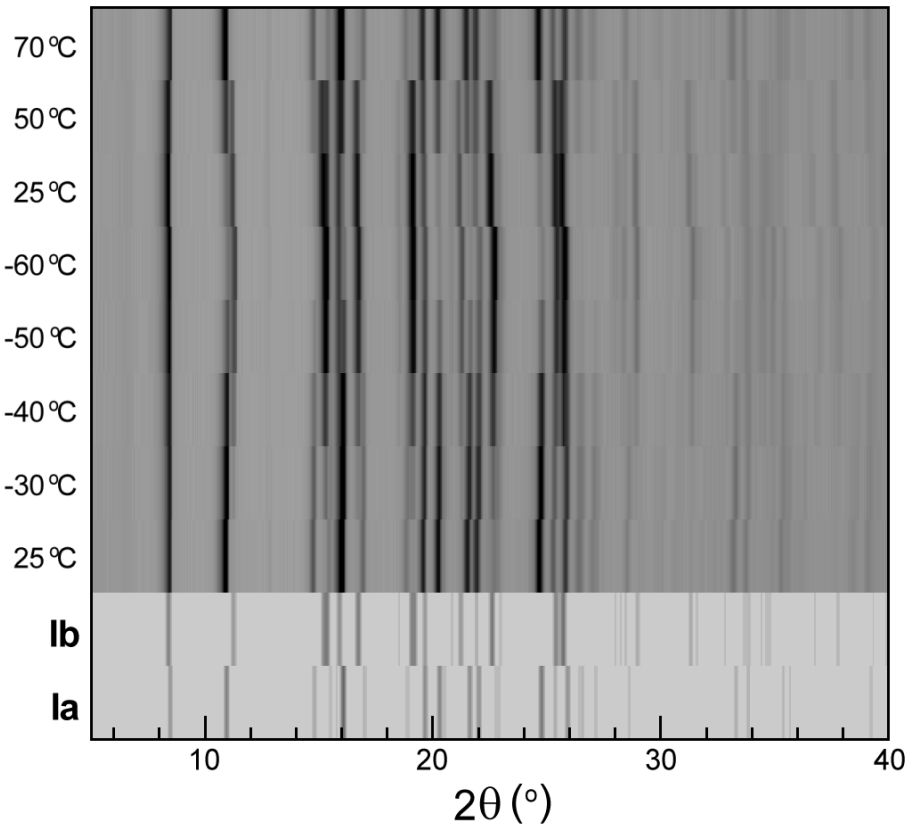


Fig. 7 Powder-3D image

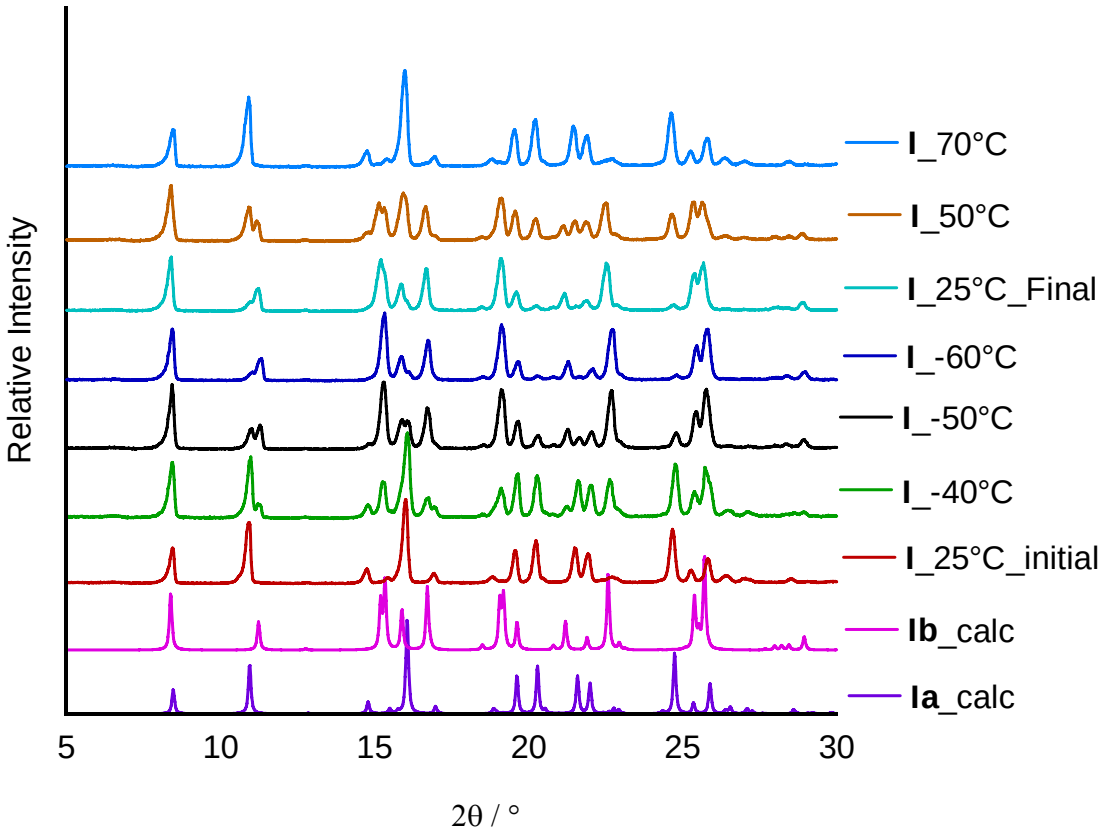


Fig. 8 Powder diffractograms of the same sample of **I** at different temperatures.