Supporting Information

Concomitant Polymorphs of the *p-tert*-Butylcalix[4]arene Analogue *p-iso*-Propylcalix[4]arene

Vincent J Smith,[a] Charl G Marais,[a] Kinga Suwińska,[b] Janusz Lipkowski,[b] Agnieszka Szumna,[c] Catharine Esterhuysen,[a] and Leonard J Barbour [a*]

[a] Department of Chemistry and Polymer Science, University of Stellenbosch, Matieland, 7602.South Africa, Fax:+27 (0)21 808 3849; Tel:+27 (0)21 808 3335; E-mail:ljb@sun.ac.za

[b] Cardinal Stefan Wyszynski University in Warsaw, Faculty of Mathematical and Natural Sciences, Wojcickiego 1/3, 01-938 Warszawa, Poland.

[c] Institute of Organic Chemistry PAS, Warsaw, Poland.

Single Crystal X-Ray Diffraction (SCXRD)

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX-II CCD area-detector diffractometer equipped with an Oxford Cryosystems Cryostream 700Plus cryostat. A multilayer monochromator with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) from a sealed tube was used.

Data reduction was carried out by means of the standard procedure using the Bruker software package SAINT and the absorption corrections and the correction of other systematic errors were performed using SADABS. The structures were solved by direct methods using SHELXS (2008) and refined using SHELXL (2008). X-Seed was used as the graphical interface for the SHELX program suite. Hydrogen atoms were placed in calculated positions using riding models.

CCDC deposit numbers contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data 75 Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC numbers are: 1048933, 1048934 and 1048935.

Table S1: Tabulated crystallographic data for Forms I_p, II_p and III_p.

Form	I_p	II_p	III_p
Formula	C40 H48 O4	C40 H48 O4	C40 H48 O4
Formula Weight	592.78	592.78	592.78
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a [Å]	9.4324(11)	24.851(3)	17.6812(15)
b [Å]	15.3488(18)	9.4124(13)	9.5252(8)
c [Å]	23.578(3)	29.215(4)	19.9837(17)
β [°]	98.751(2)	103.211(2)	98.363(2)
V [Å^3]	3373.8(7)	6652.8(15)	3329.8(5)
Z	4	8	4
D_{calc} [g/cm^3]	1.167	1.184	1.183
Mu(MoKa) [/mm]	0.074	0.075	0.074
F(000)	1280	2560	1280
Crystal Size [mm]	0.10 x 0.12 x 0.20	0.06 x 0.10 x 0.23	0.06 x 0.10 x 0.24
Temperature (K)	100(2)	100(2)	100(2)
Radiation [Å] MoKa	0.71073	0.71073	0.71073
Theta Min-Max [°]	1.6, 28.3	1.4, 28.3	1.7, 26.0
Dataset	-11: 6 ; -20: 16 ; -30: 28	-33: 32 ; -12: 12 ; -37: 37	-12: 21 ; -11: 11 ; -24: 21
Tot., Uniq. Data, R(int)	14481, 7453, 0.065	36604, 7870, 0.028	17118, 6530, 0.048
Observed data [I > 2.0 sigma(I)]	3730	6706	4449
N_{ref}, N_{par}	7453, 409	7870, 445	6530, 419
R, wR2, S	0.0658, 0.1775, 0.95	0.0601, 0.1600, 1.02	0.0529, 0.1363, 1.03
Max. and Av. Shift/Error	0.00, 0.00	0.00, 0.00	0.00, 0.00

Min. and Max. Resd. Dens. [e/Å^3]	-0.28, 0.25	-0.29, 0.50	-0.28, 0.29

Differential Scanning Calorimetry (DSC)

DSC thermograms were obtained using a TA Instruments Q20 differential scanning calorimeter. Heating rates of 10, 15 and 20 K min^{-1} was used in the range 25 to 315 °C. The sample was purged with N_2 at flow rate 50 mL min^{-1}. Sample sizes ranged between 4 and 8 mg.

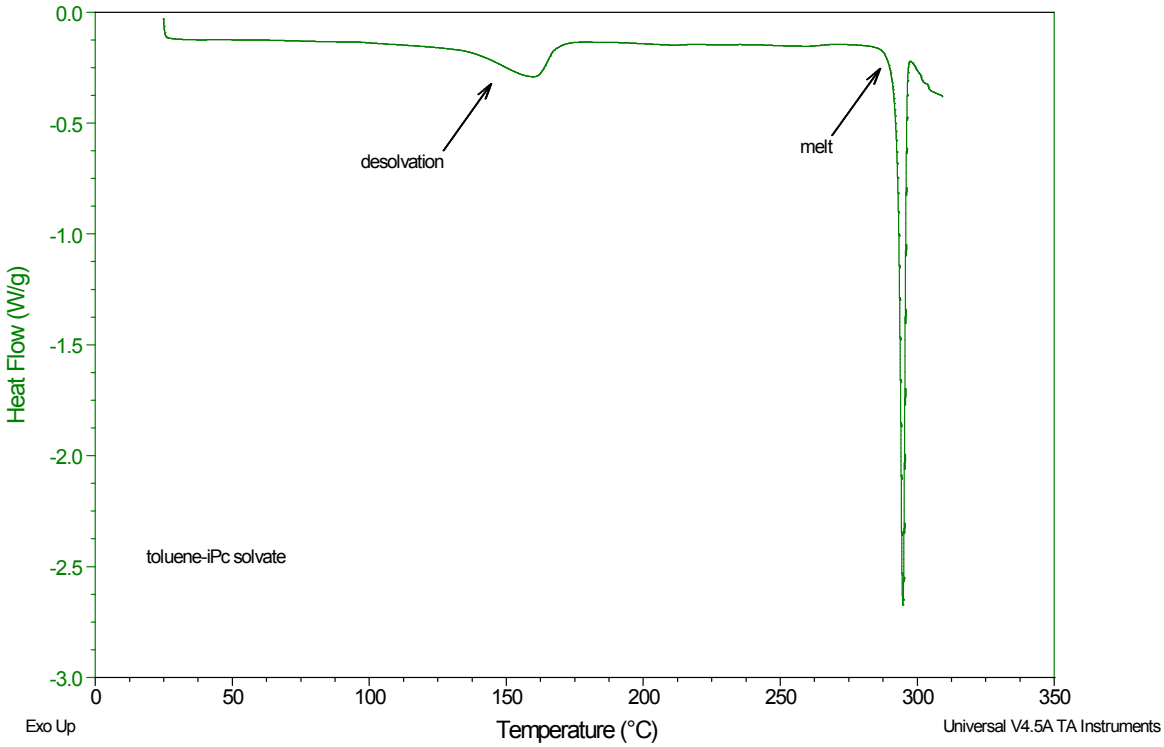
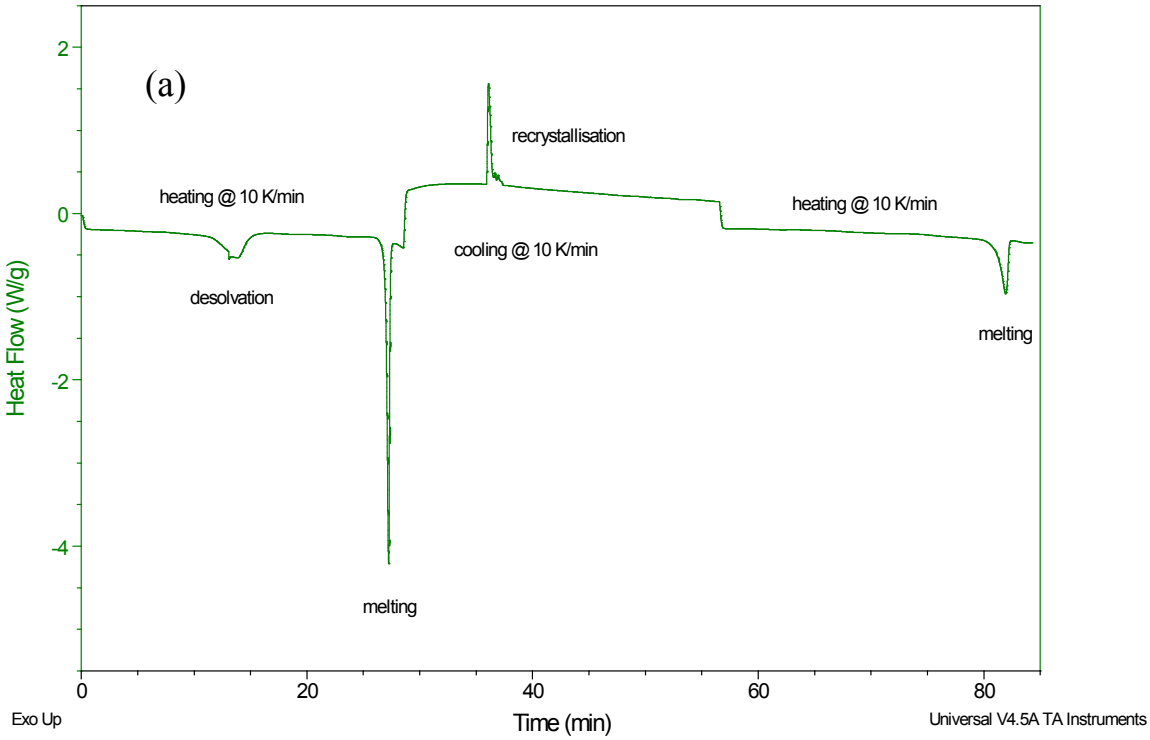
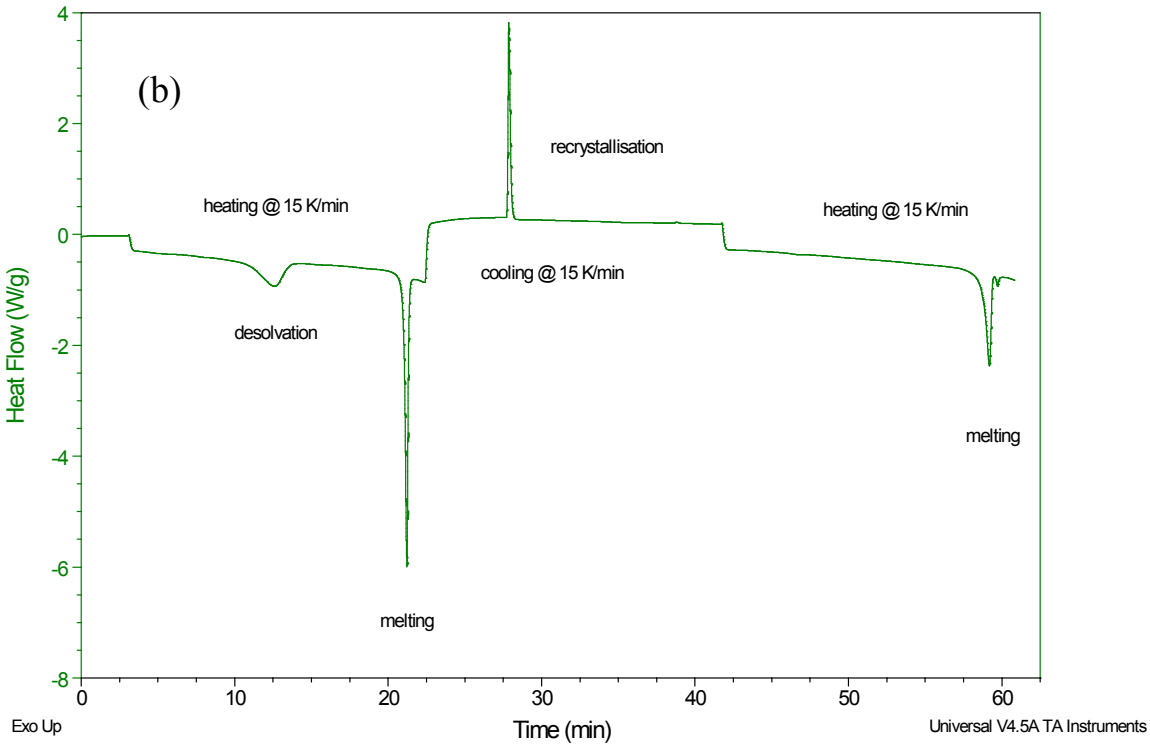


Figure S1. Thermogram of the toluene-*p-iso*-propylcalix[4]arene solvate.


(a)
recrystallisation
heating @ 10 K/min
heating @ 10 K/min
cooling @ 10 K/min
desolvation
melting
melting
Heat Flow (W/g)
2
0
-2
-4
0
20
40
60
80
Time (min)
Exo Up
Universal V4.5A TA Instruments


(b)
recrystallisation
heating @ 15 K/min
heating @ 15 K/min
cooling @ 15 K/min
desolvation
melting
melting
Heat Flow (W/g)
4
2
0
-2
-4
-6
-8
0
10
20
30
40
50
60
Time (min)
Exo Up
Universal V4.5A TA Instruments

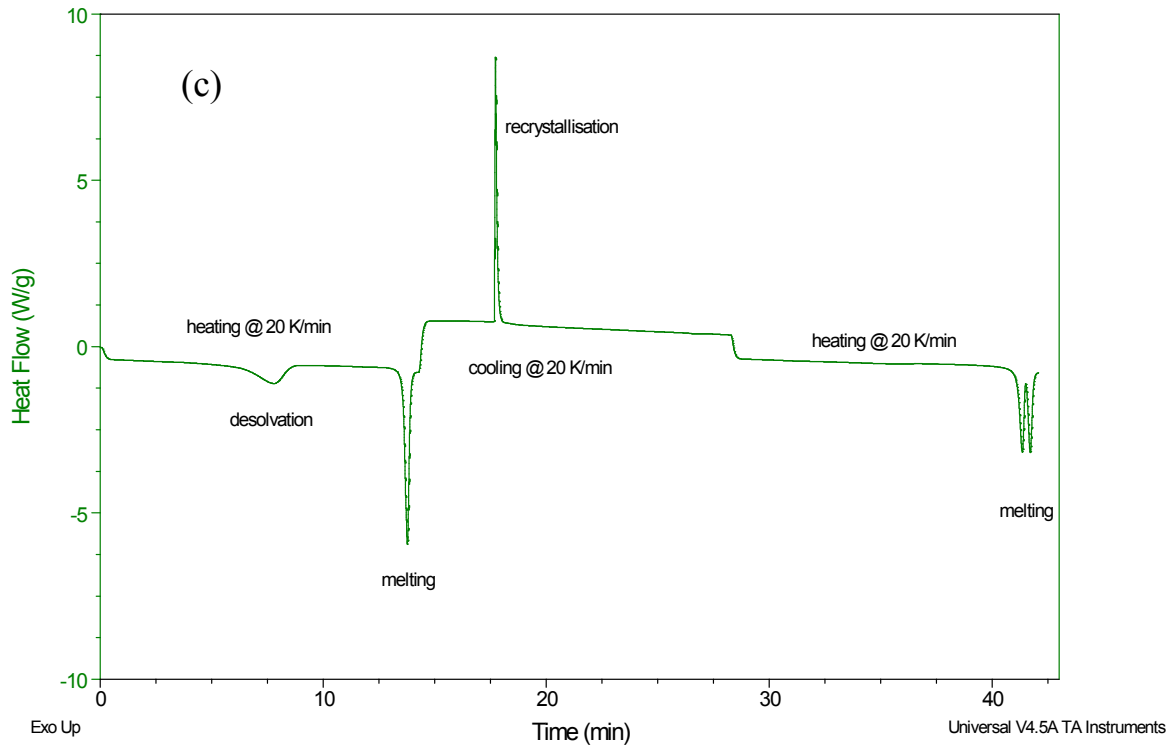


Figure S2. Thermograms of the *i*Pc-toluene solvate carried out at various heating rates. (a) 10 K min^{-1}, (b) 15 K min^{-1}, and (c) 20 K min^{-1}.

Powder X-Ray Diffraction (PXRD)

The diffractograms were recorded with a Bruker D2 PHASER with Lynxeye 1D detector and Ni-filtered copper Kα radiation (30kV, 10mA generator parameters; restricted by a 1.0 mm divergence slit and a 2.5° Soller collimator) with a 0.02° step width.

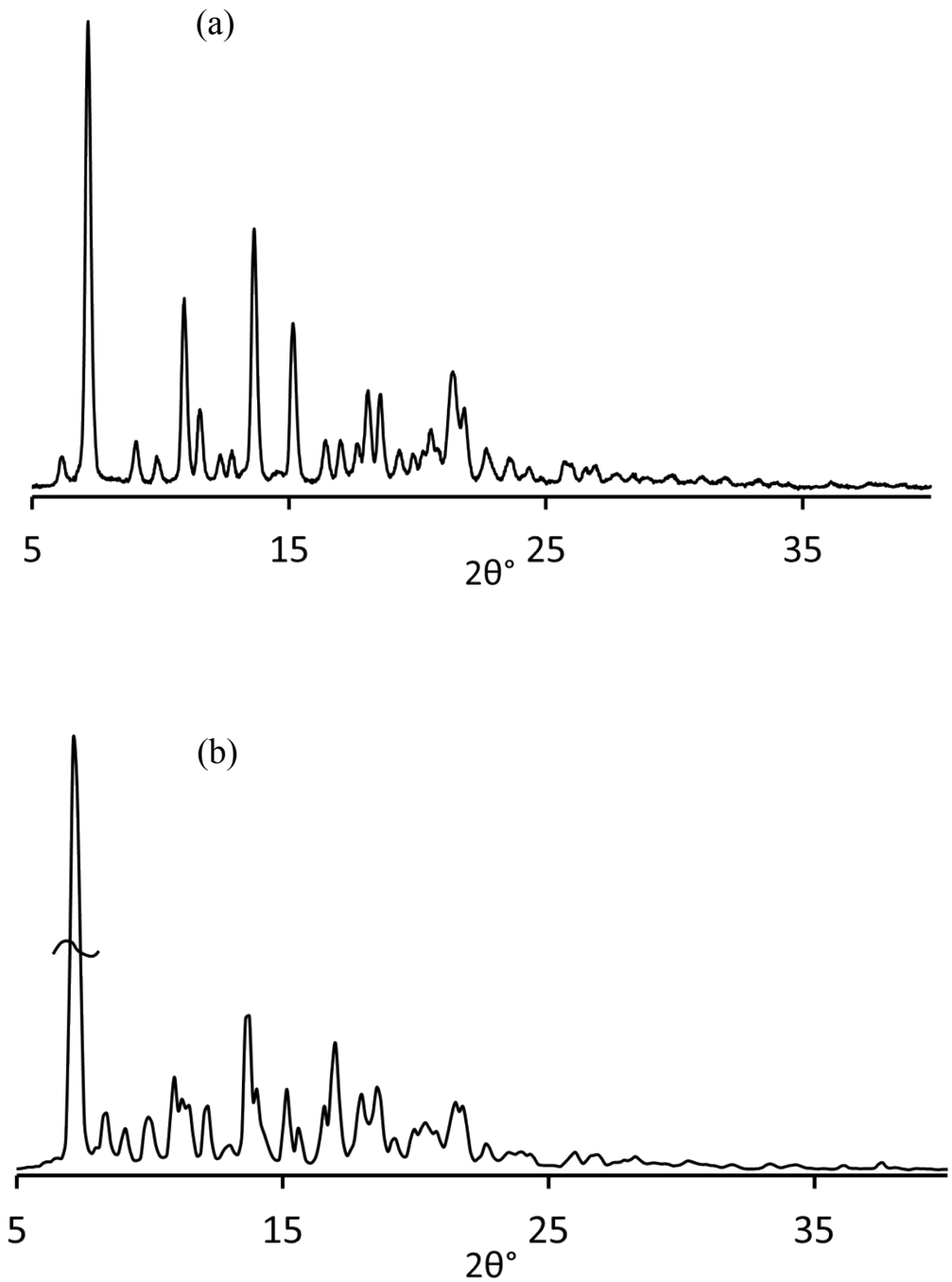
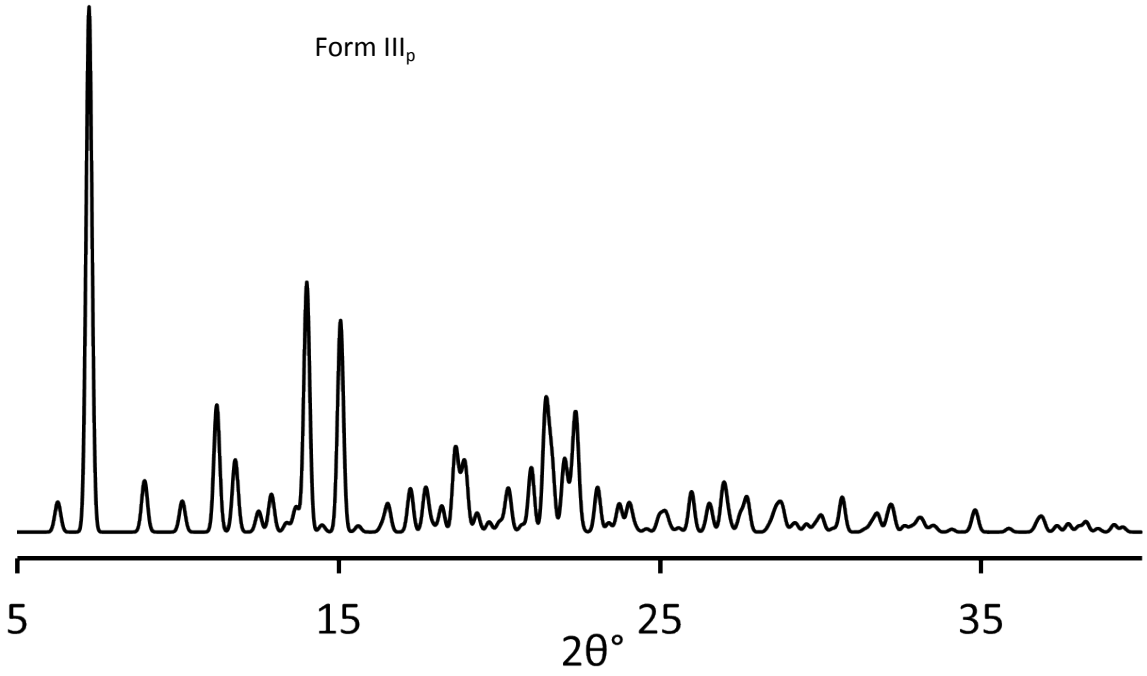
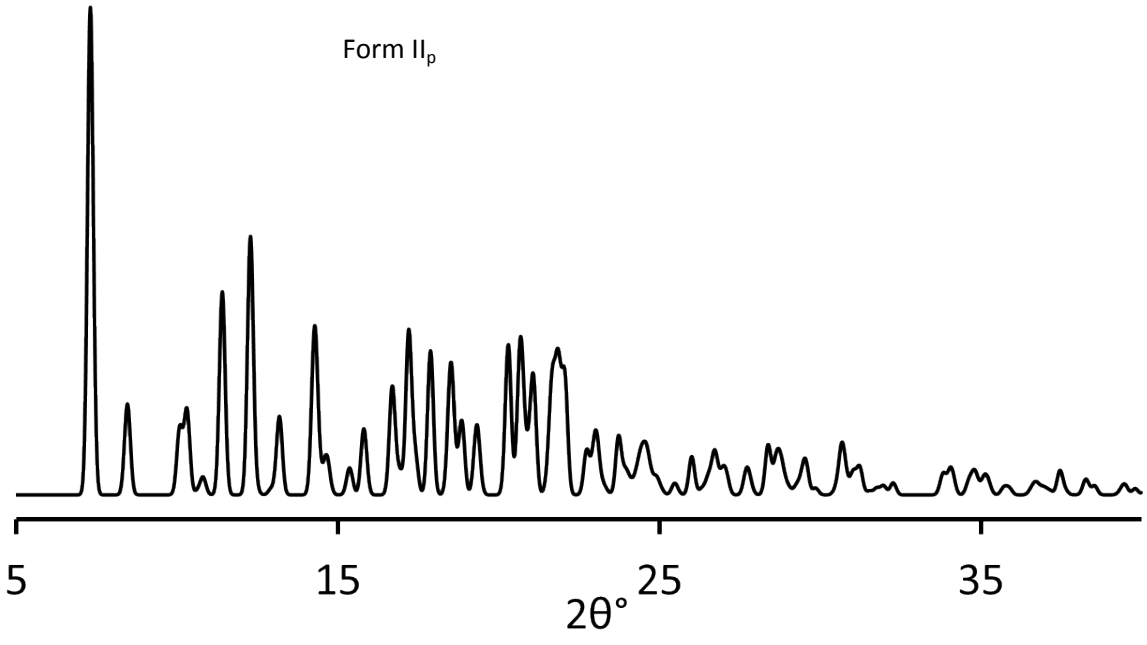


Figure S3. PXRD profiles of the recrystallized phases from the melt. (a) Form III_p obtained from the melt of the *i*Pc-toluene solvate at heating rate of 10 K min^{-1}, (b) A mixture of forms II_p and III_p obtained from the melt of the *i*Pc-toluene solvate at heating rate of 20 K min^{-1}. The PXRD for the

recrystallized phases obtained from melting the *i*Pc-toluene solvate at heating rate of 15 K min^{-1} matched form III_p as the quantity of form II_p was very small.

Calculated PXRDs





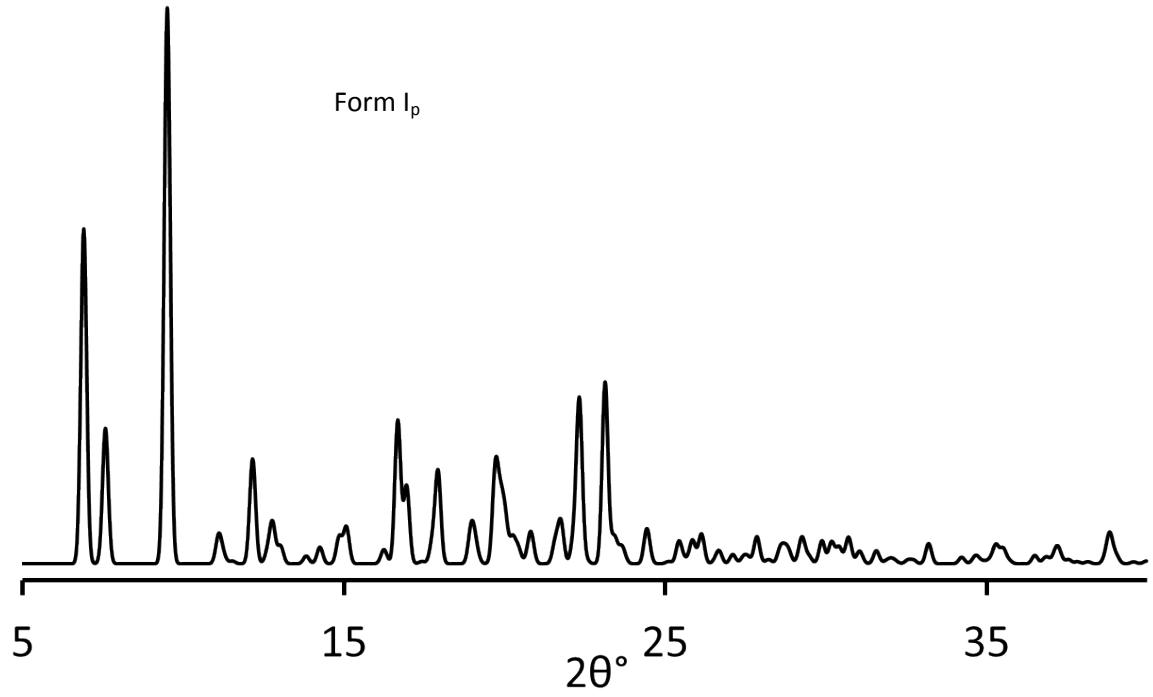


Figure S4. Calculated PXRD profiles for the three polymorphs of *i*Pc, with form III_p at the top, form II_p in the middle, and form I_p at the bottom.