Supporting information

Solid-state stability of Z' < 1 and Z' = 2 polymorphs of *N,N,N',N'*-tetrabenzylethylenediamine: a combined experimental and theoretical study

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Figure captions and tables.

Figure S1. (a) Experimental powder XRD patterns of **L** crystallized from methanol, with phases α (black dots) and β (red dots) indicated. Simulated XRPD patterns of phases β (b) and α (c).

Figure S2. IR spectrum of phase α, β and γ. (Red: α/β; Green: γ).

Figure S3. Powder XRD recorded at different temperatures for a mixture of phases α and β.

Figure S4. DSC of phase α/β.

Figure S5. DSC of phase γ.

Figure S6. Powder XRD patterns for (a) DSC experiment stopped at 94 ºC; (b) powder XRD simulated form single crystal data of γ polymorph.

Figure S7. ORTEP diagram of the β phase.

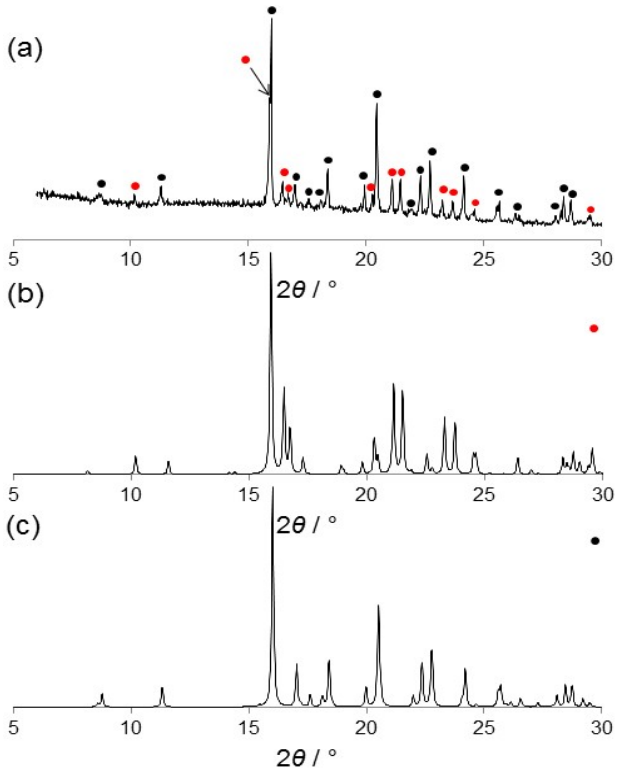

Figure S1. (a) Experimental powder XRD patterns of **L** crystallized from methanol, with phases α (black dots) and β (red dots) indicated. Simulated XRPD patterns of phases β (b) and α (c).

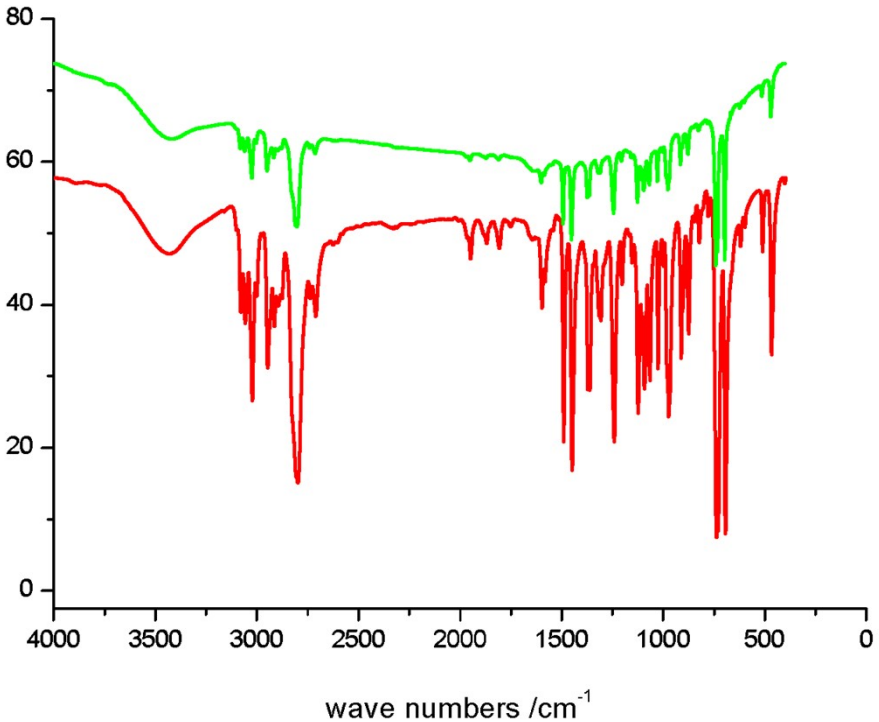

Figure S2. IR spectrum of phase α, β and γ. (Red: α/β; Green: γ).

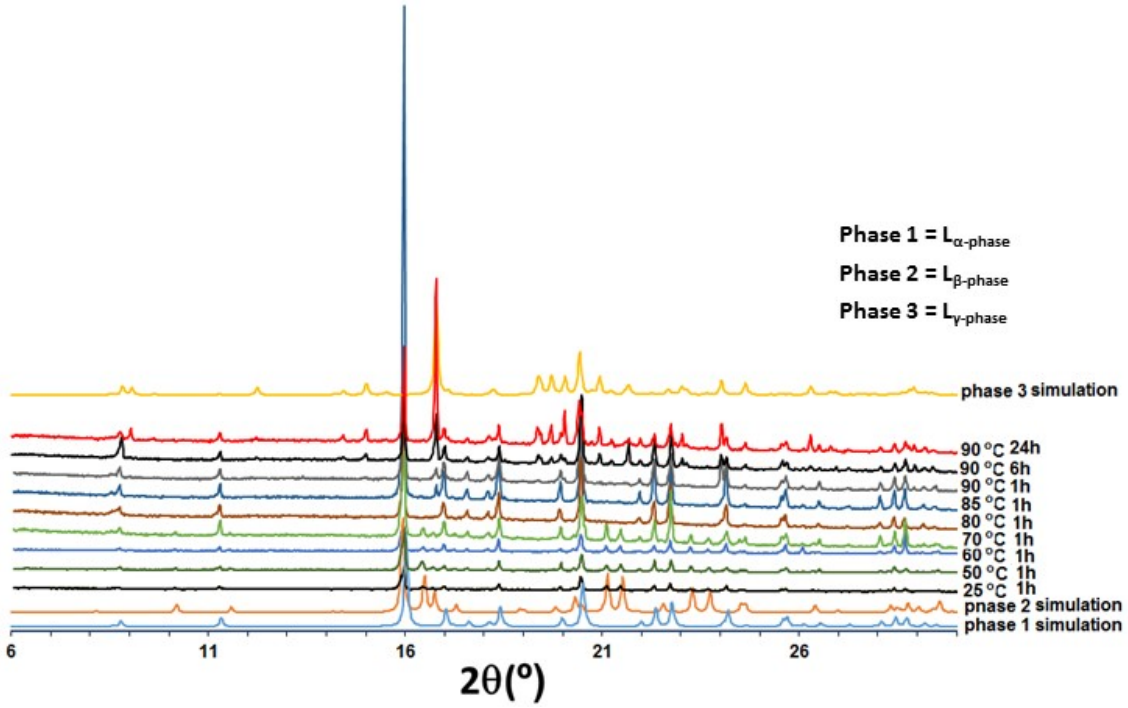

Figure S3. Powder XRD recorded at different temperatures for a mixture of phases α and β.

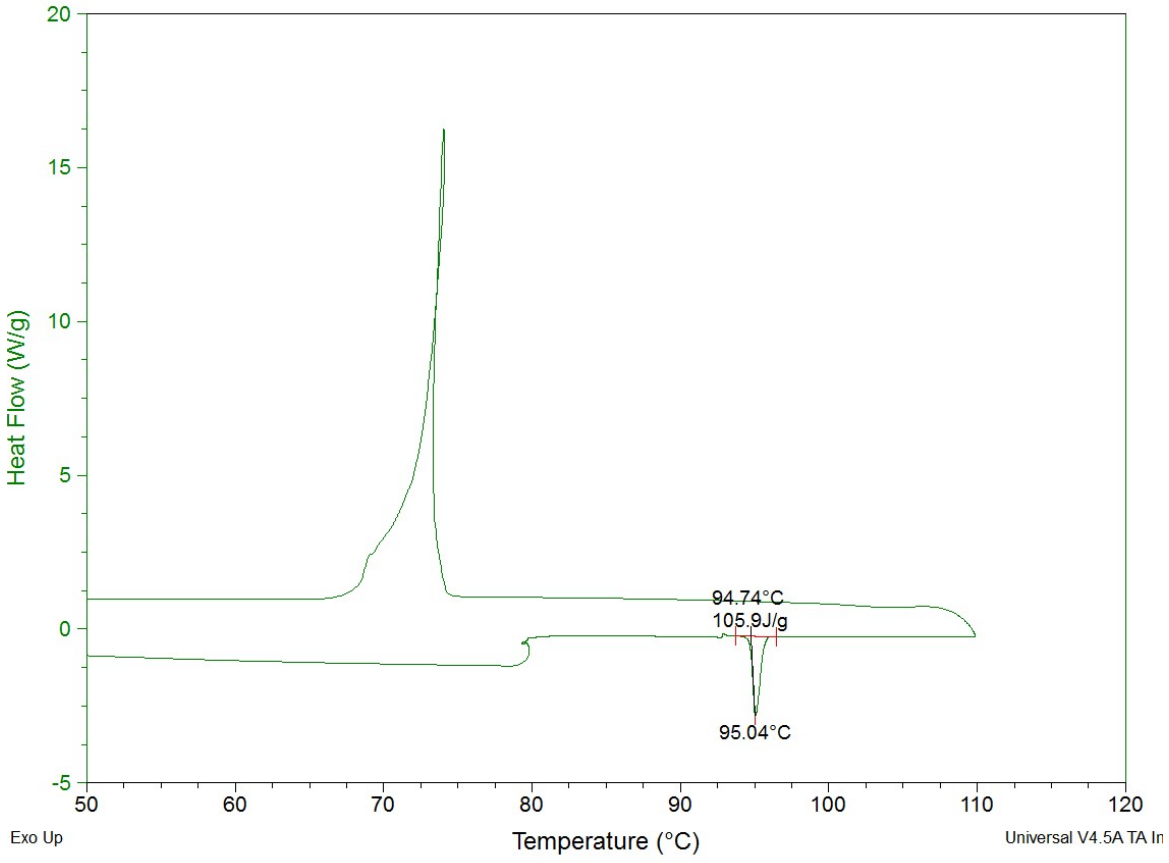

Figure S4. DSC of phase α/β.

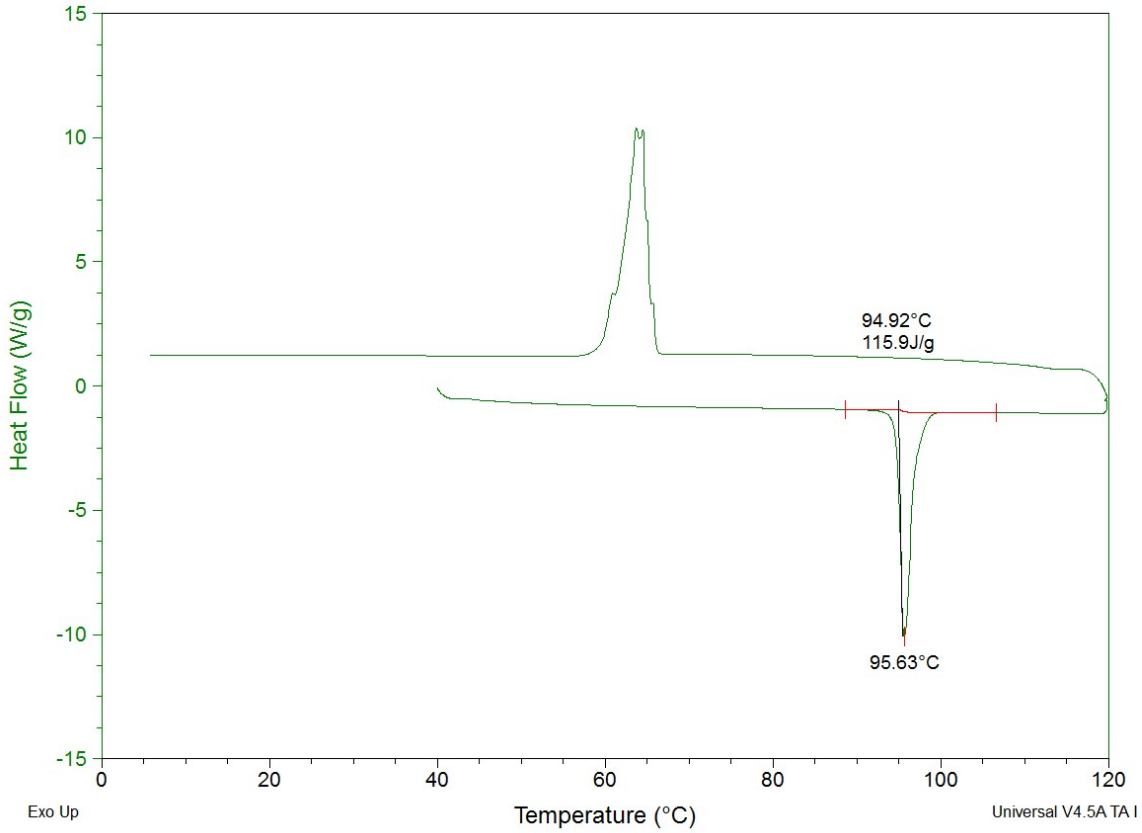

Figure S5. DSC of phase γ.

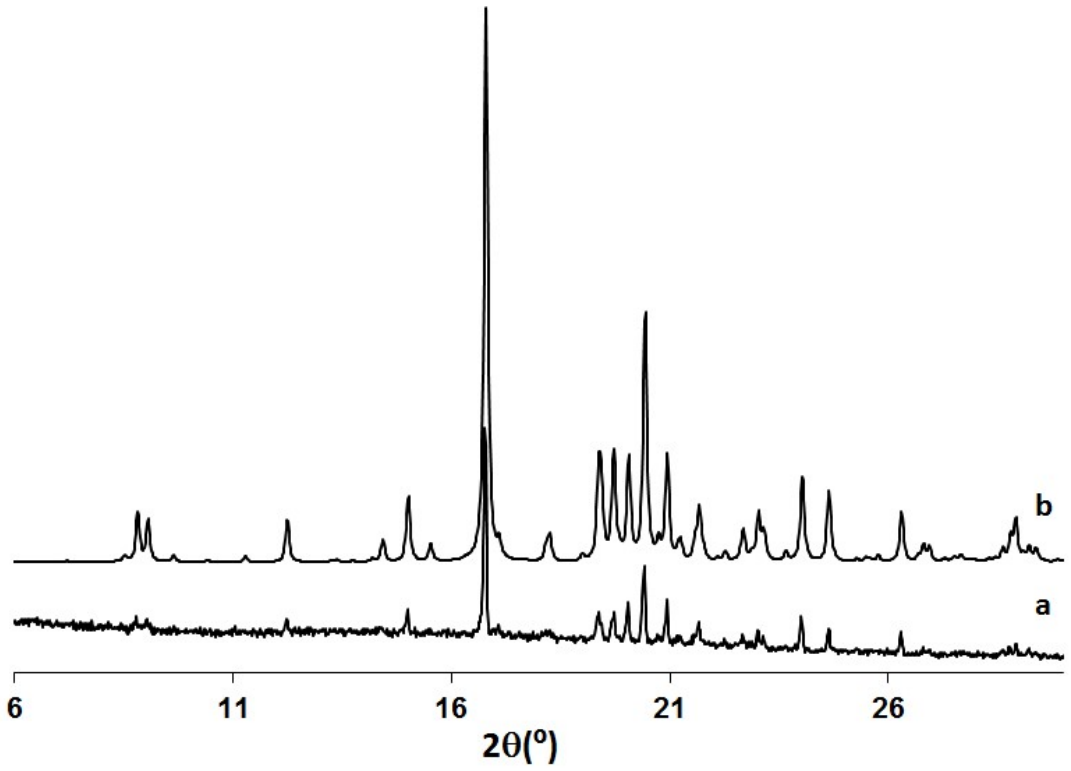

Figure S6. Powder XRD patterns for (a) DSC experiment stopped at 94 ºC; (b) powder XRD simulated form single crystal data of γ polymorph.

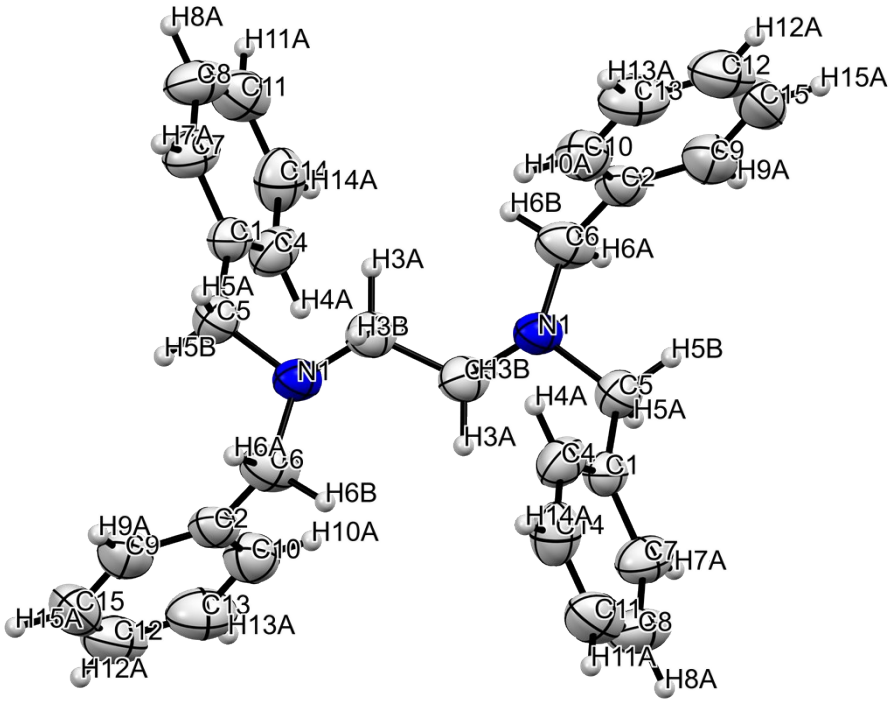

Figure S7. ORTEP diagram of the β phase.

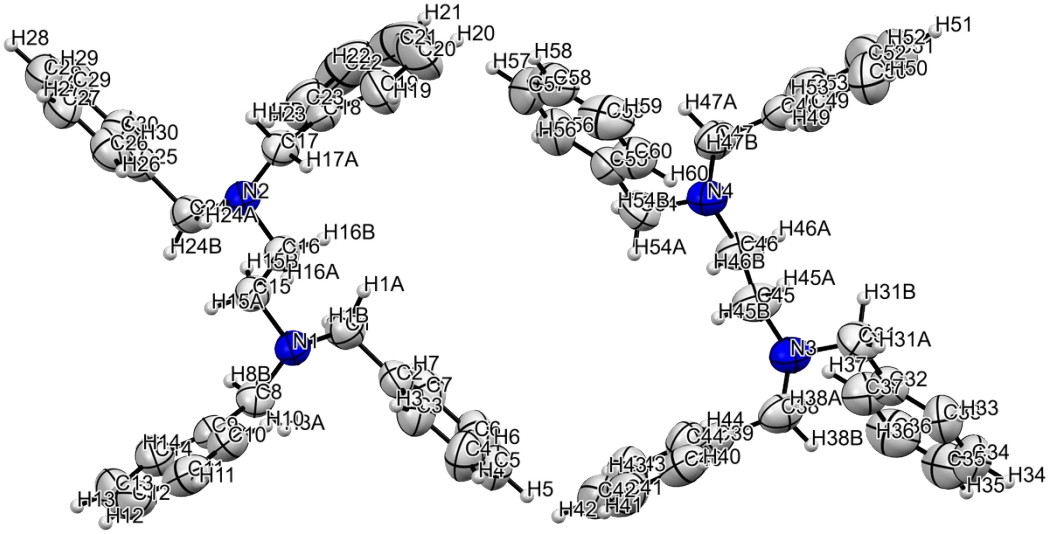

Figure S8. ORTEP diagram of the γ phase.

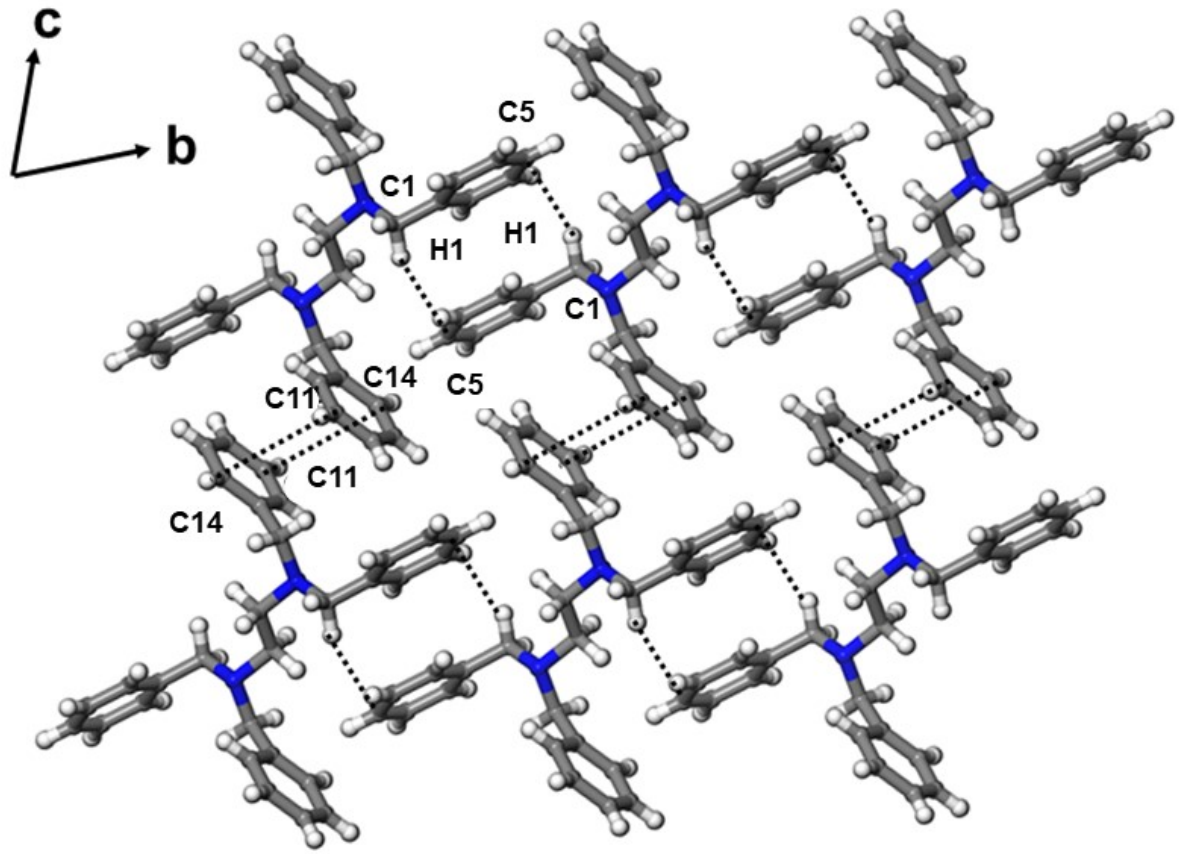

Figure S9. Electrostatic interactions in the β phase in dashed lines showed in Table S1.

Table S1. Electrostatic interactions shown in Figure S9 in the β polymorph.

D-H···A	D-H(Å)	H···A/π···π(Å)	D···A(Å)	D-H···A(°)
C1-H1····C5	0.97	2.85	3.63	138
C14···C11 (π···π)		3.57		

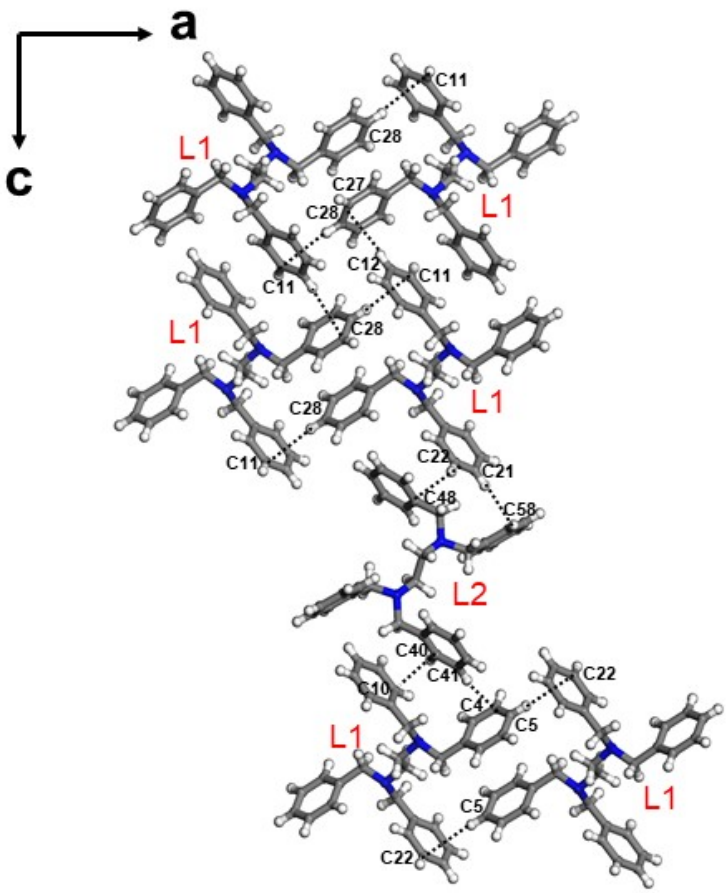

Figure S10. Electrostatic interactions in the γ phase in dashed lines showed in Table S2.

Table S2. Electrostatic interactions in the γ polymorph shown in Figure S10.

D-H···A	D-H(Å)	H···A (Å)	D···A(Å)	D-H···A(°)
C28-H28···C11	0.93	2.94	3.63	138
C12-H12···C27	0.93	2.98	4.08	175
C22-H22···C48	0.93	3.09	3.95	154
C21-H21···C58	0.93	2.82	3.75	176
C40-H40···C10	0.93	3.12	3.98	154
C41-H41···C4	0.93	2.98	3.87	160
C5-H5···C22	0.93	3.02	3.95	174

Density Functional Theory Calculations

Molecular modelling studies are performed in the crystalline phase, (*i.e.*, under periodical conditions). The GGA PBE functional[1] is adopted together with explicit van der Waals corrections[2] to improve the description of van der Waals interactions.[3] A numerical double zeta numerical basis set centered on atoms (including polarisation functions on all atoms), roughly comparable with the usual 6-31G** gaussian basis, has been employed. The DMol[3] package[4] was employed for all the calculations.
The geometries of the crystalline assemplies have been obtained from experimental X-ray determined structures and optimized by fixing the cells under symmetry restrain conditions.

DFT optimized coordinates in α, β and γ -phases.

Polymorph alpha:

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TER 33

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TER 33

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ATOM 106 H51 MOL 2 37.530 2.385 5.216 1.00 0.18 H
ATOM 107 C52 MOL 2 36.216 4.078 5.069 1.00 0.15 C
ATOM 108 H52 MOL 2 36.731 4.642 5.830 1.00 0.18 H
ATOM 109 C53 MOL 2 35.083 4.617 4.441 1.00 0.10 C
ATOM 110 H53 MOL 2 34.729 5.598 4.715 1.00 0.13 H
ATOM 111 C54 MOL 2 31.629 4.401 0.916 1.00 0.09 C
ATOM 112 AH54 MOL 2 31.629 4.495 -0.170 1.00 0.11 H
ATOM 113 BH54 MOL 2 31.189 5.320 1.326 1.00 0.11 H
ATOM 114 C55 MOL 2 30.768 3.216 1.315 1.00 0.08 C
ATOM 115 C56 MOL 2 29.558 3.405 2.005 1.00 0.11 C
ATOM 116 H56 MOL 2 29.243 4.406 2.264 1.00 0.13 H
ATOM 117 C57 MOL 2 28.761 2.304 2.358 1.00 0.13 C
ATOM 118 H57 MOL 2 27.841 2.451 2.902 1.00 0.15 H
ATOM 119 C58 MOL 2 29.161 1.007 2.011 1.00 0.13 C
ATOM 120 H58 MOL 2 28.541 0.164 2.271 1.00 0.15 H
ATOM 121 C59 MOL 2 30.373 0.810 1.331 1.00 0.12 C
ATOM 122 H59 MOL 2 30.692 -0.190 1.079 1.00 0.14 H

ATOM	123	C60	MOL	2	31.169	1.909	0.988	1.00	0.09	C
ATOM	124	H60	MOL	2	32.102	1.761	0.470	1.00	0.11	H
ATOM	125	N1	MOL	2	25.229	9.413	-1.124	1.00	0.06	N
ATOM	126	N2	MOL	2	23.552	6.711	0.987	1.00	0.06	N
ATOM	127	N3	MOL	2	35.322	5.488	-1.418	1.00	0.07	N
ATOM	128	N4	MOL	2	33.040	4.242	1.383	1.00	0.07	N
TER	129									

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