Supplementary Material (ESI) for New Journal of Chemistry

Cocrystal of 4-oxopimelic acid and 4,4'-bipyridine: polymorphism and solid-state transformation

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Materials and Methods

Materials. All chemicals were obtained from Sigma-Aldrich and used without further purification. Solvents (p.a. grade) were purchased from Kemika, Zagreb.

Methods.

IR spectra were recorded on PerkinElmer *Spectrum RXI* FT-IR spectrometer as KBr pellets (4000-400 cm^{-1} range, 2 cm^{-1} step).

DSC measurements were performed on the Mettler–Toledo DSC823^e calorimeter with STARe SW 9.01 in the range of 25–600 °C (heating rate 5 °C/min) under nitrogen stream.

X-ray Diffraction Experiments. The single-crystal X-ray data were collected by Oxford Diffraction Xcalibur CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation at 293 K using ω-scans at the crystal to detector distance of 50 or 60 mm. Details of data collection and crystal structure refinement are presented in Table 1. Programs CrysAlis CCD and CrysAlis RED[1] were employed for data collection, cell refinement and data reduction. The structures were solved by direct methods. Refinement procedure by full-matrix least squares methods based on F^2 values against all reflections included anisotropic displacement parameters for all non-H atoms. The positions of hydrogen atoms residing on carbon atoms were positioned geometrically and refined applying the riding model [C–H = 0.95–0.98 Å and with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2$ or $1.5U_{\mathrm{eq}}(\mathrm{C,N})$]. The position of the hydroxyl group hydrogen atoms were obtained from the difference Fourier map and were included in the refinement process with isotropic thermal parameter [O–H =0.91(3)-0.94(2) Å]. Calculations were performed with SHELXS97[2] and SHELXL97[3] (both operating under the WinGX[4] program package). Geometry calculations were done using PLATON[5] and PARST[6], and the molecular graphics were done with ORTEP[7] and Mercury[8]. Selected bond distances and valence angles are listed in Table S2.

X-ray powder diffraction experiments were performed on a Philips PW 3710 diffractometer, Cu$K\alpha$ radiation, flat plate sample on a zero background in Bragg-Brentano geometry, tension 40kV, current 40 mA. The patterns were collected in the angle region between 4θ and 50θ (2θ) with a step size of 0.02° and 1.0 s counting per step.

Syntheses

To a solution of 4-oxopimelic acid (**opa**, 0.050 g, 0.3 mmol) in 2 mL of appropriate alcohol 4,4'-bipyridine (**bipy**) was added (0,045 g, 0.3 mmol). Crystalline product was collected after two days standing at room temperature. Form I was obtained from ethanol (0.54 g, 56 %); Form II from methanol (0.60 g, 63 %).

Reaction was repeated in methanol with different stoichiometries of starting compounds. When an excess of **opa** was added (**opa**:**bipy** = 2:1, 4:1, 6:1) to the solution of **bipy**, Form II was collected with similar yields. Due to the poor solubility of **opa**, the 6:1 ration of reactants was the highest ratio tested.

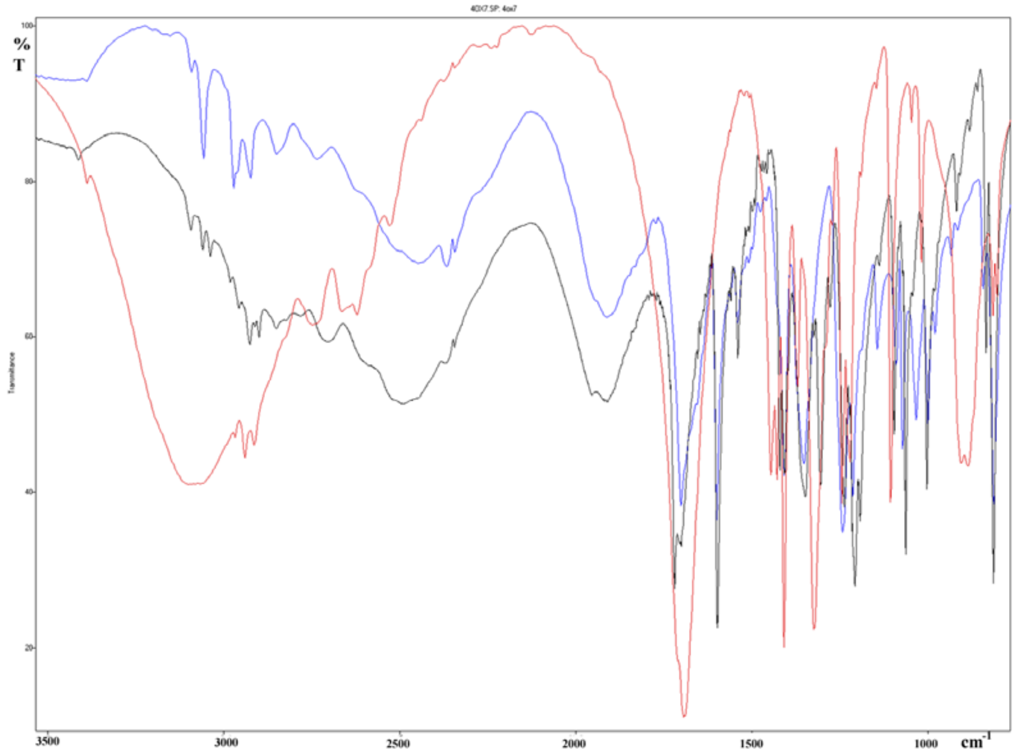
When an excess of **bipy** was added, no product was obtained, possibly due to the deprotonation of **opa**.

Polymorph screening experiments

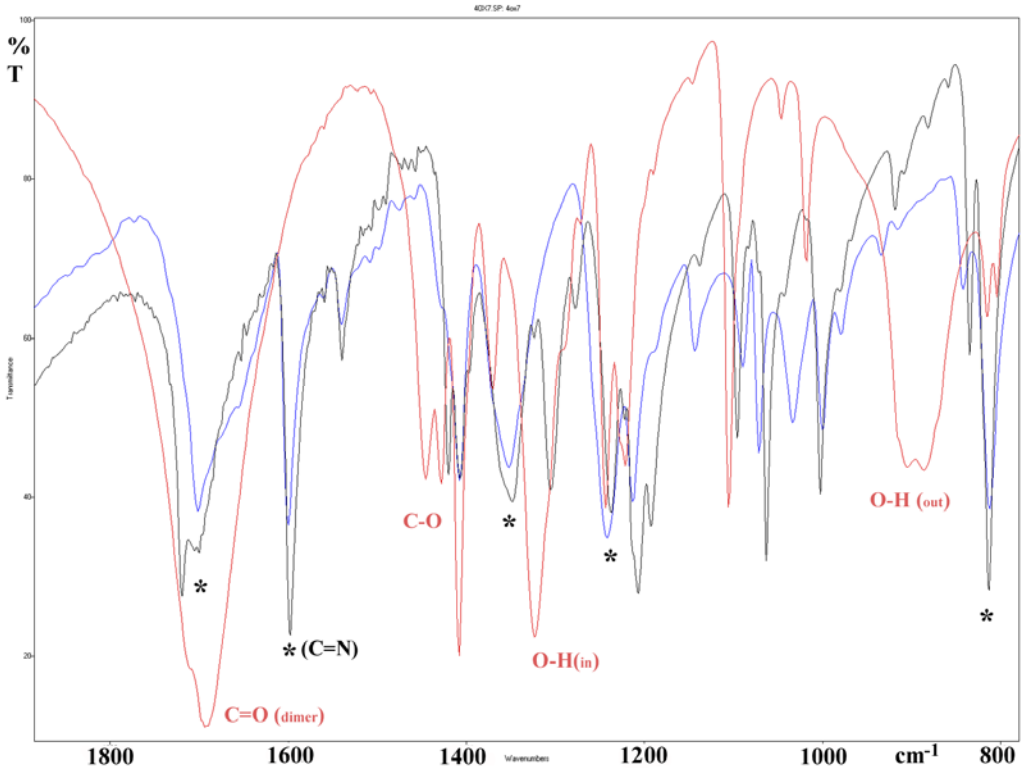
Form I (space group: $P2_1/n$) was obtained from ethanol, acetone, acetonitrile, water and dimethyl formamide/acetone (1:1) mixture.

Reactions from methanol, propanol, hexanol, benzonitrile, ethyl acetate, dimethyl sulfoxide and dimethyl formamide afforded Form II (space group: $C2/c$).

Infrared Spectroscopy



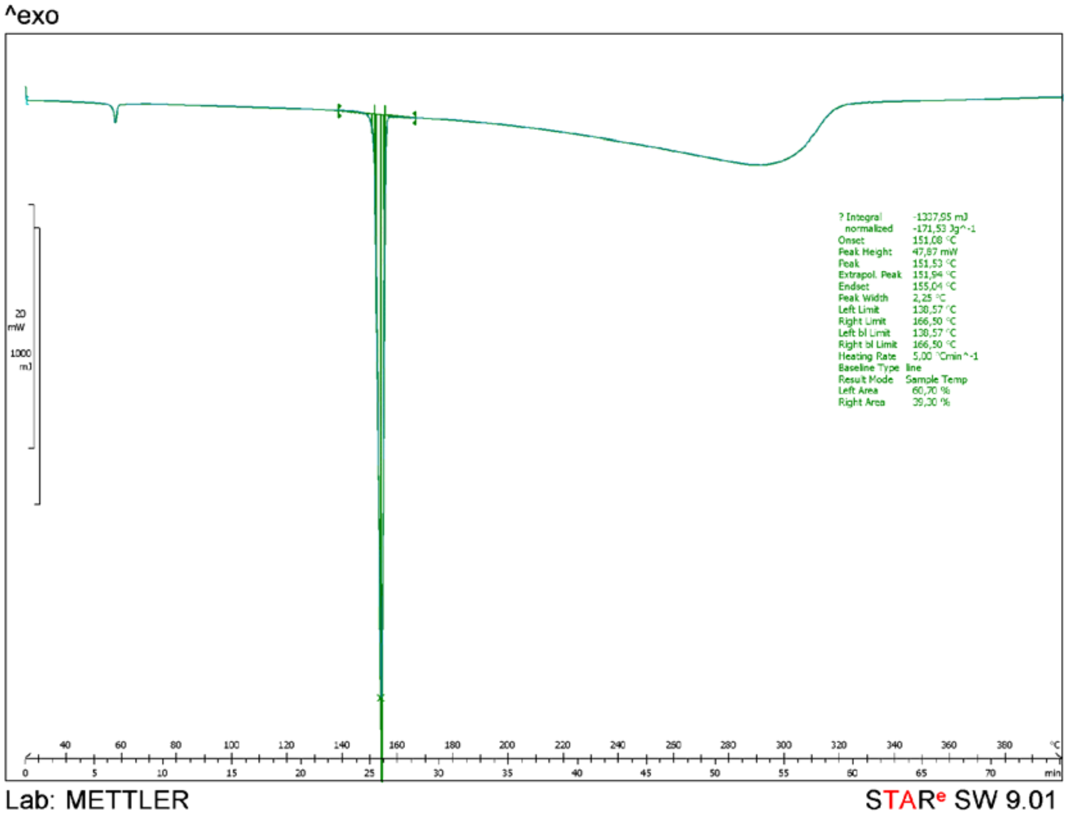
(a)



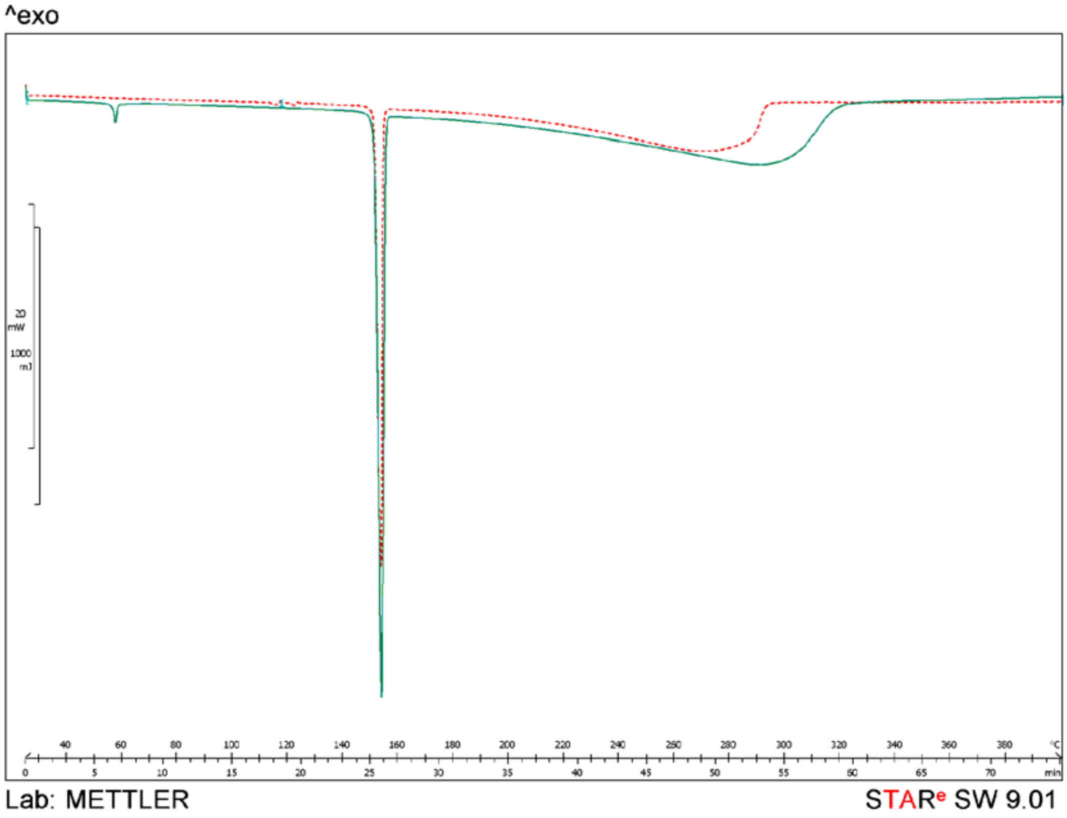
(b)

Figure S1. a) Infrared spectra of **opa** (red), Form I (black) and Form II (blue) in the range of 3500–800 cm^{-1}; b) Infrared spectra of **opa** (red), Form I (black) and Form II (blue) in the range of 1800–800 cm^{-1}. Bands characteristic for dimeric O–H···O hydrogen bond in **opa** are designated in red. **Opa·bipy** bands important for discussion are denoted with asterisk.

Thermal experiments



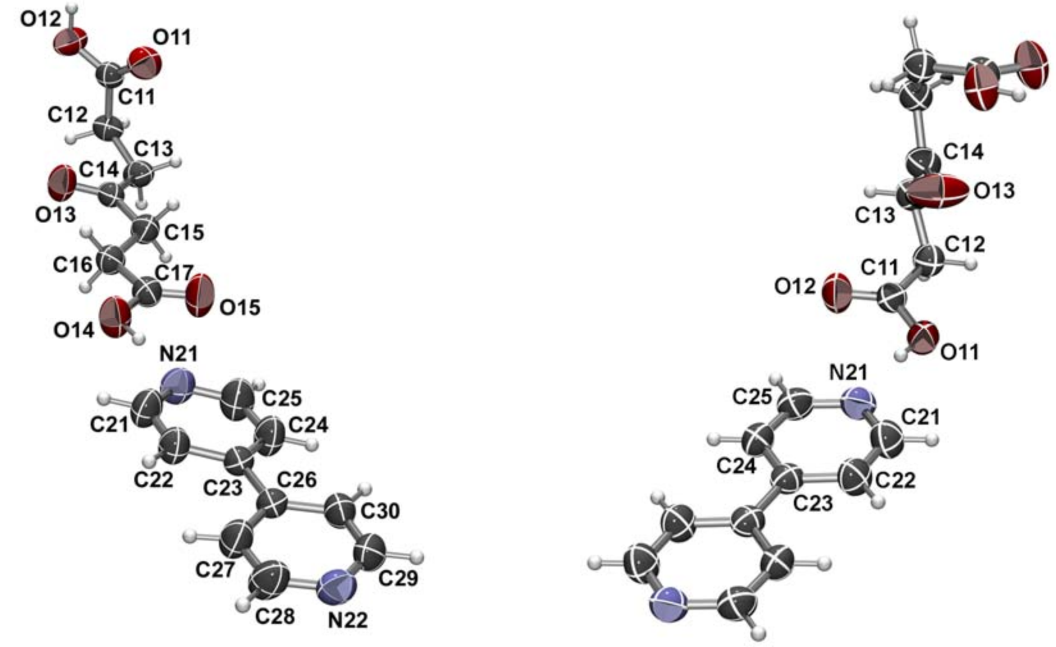
(a)



(b)

Figure S2. a) DSC curves of Form II and b) overlay of both forms (Form I – orange, Form II – green).

X-ray crystallography



a) **b)**

Figure S3. ORTEP-POV-Ray rendered view of opa·bipy polymorphs with atom numbering. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are presented as spheres of arbitrary small radii; a) Form I (*P*21/c) and b) Form II (*C*2/c).

Table S1. C–H···O interactions in the crystal structures of all three polymorphs

	d(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	∠(D–H···A)/°
		Form I		
C21–H21···O13^{i}	0.93	2.46	3.260 (3)	145
C27–H27···O15^{ii}	0.93	2.46	3.150(3)	131
C29–H29···O13^{iii}	0.93	2.57	3.236(2)	129
		Form II		
C13–H13B···O11^{iv}	0.97	2.54	3.378(3)	145
C22–H22···O12^{v}	0.93	2.55	3.434(3)	159
C24–H24···O12^{vi}	0.93	2.60	3.483(3)	159

i = 1–*x*, 1–*y*, 1–*z*; *ii* = –1/2+*x*, 3/2–*y*, –1/2+*z*; *iii* = –1+*x*, 1+*y*, *z*.
iv = 1/2+*x*, –1/2+*y*, *z*; *v* = *x*, 1+*y*, *z*; *vi* = 1–*x*, 1–*y*, –*z*.

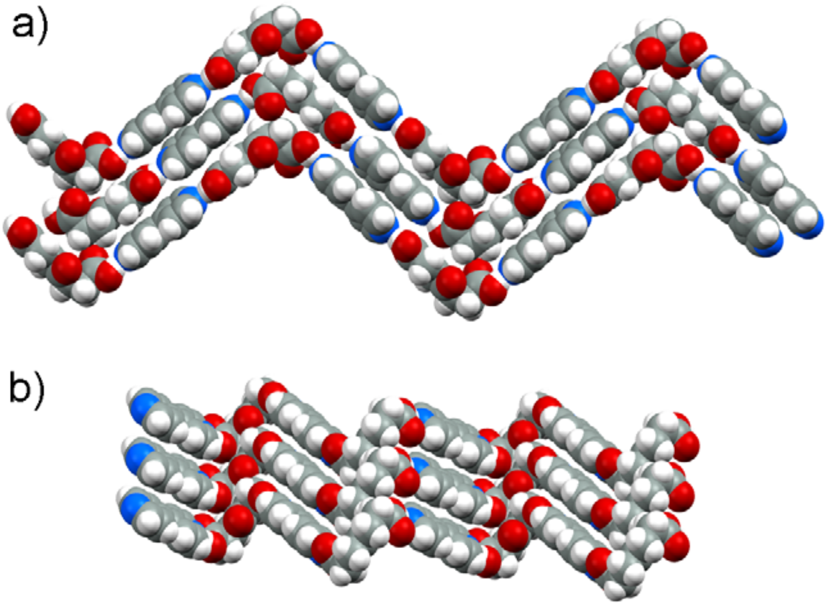


Figure S4. Space-filling model of hydrogen bonded zig-zag chains in a) Form I and b) Form II.

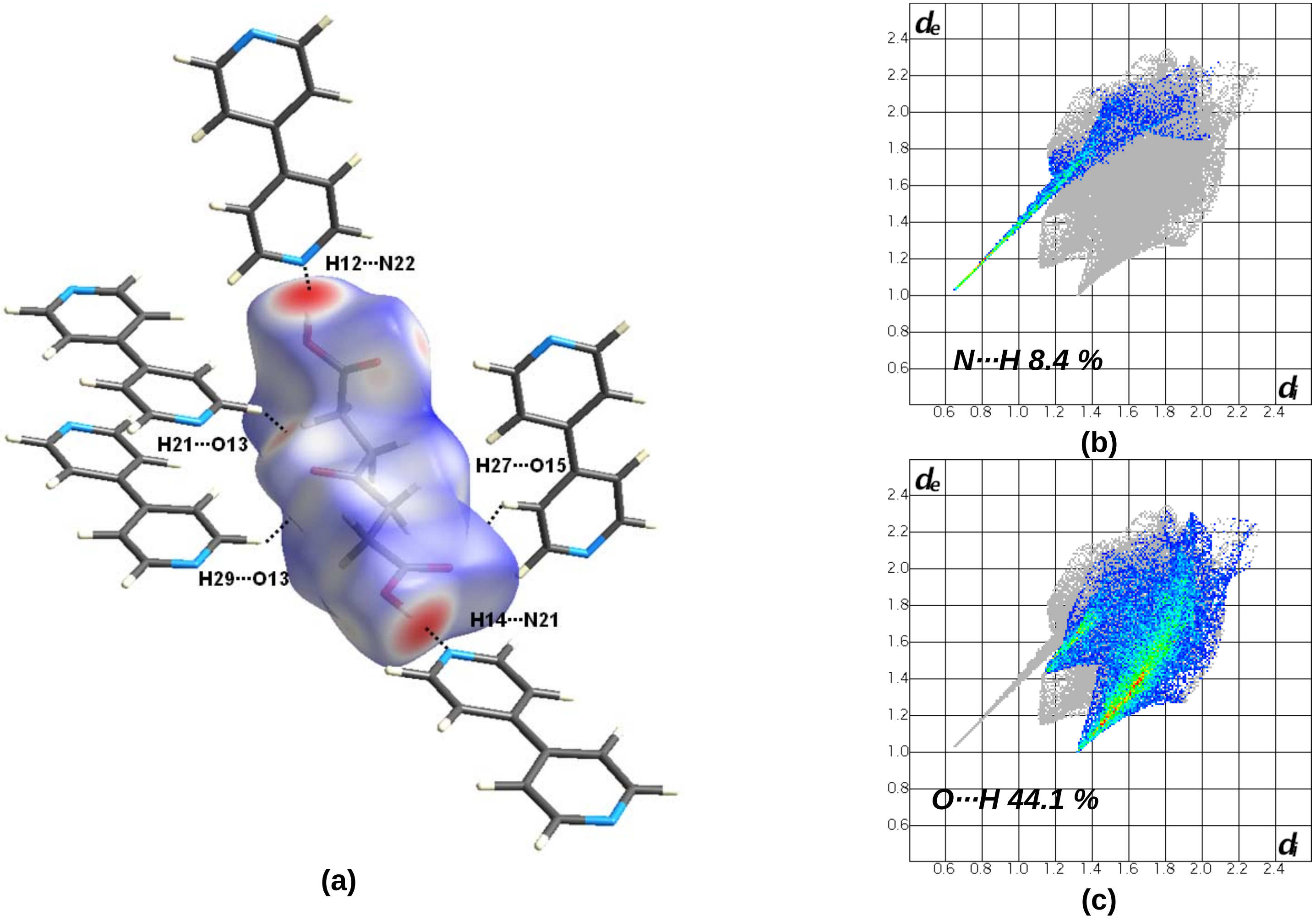


Figure S5. (a) Hirshfeld surface[9] for **opa** in Form I mapped with d_{norm} over the range –0.8 to 1.3. Close contacts with neighbouring molecules are presented with dashed lines;

(b) and (c) fingerprint plots for **opa** in Form I, broken down into contributions from specific pairs of atom-types. The grey shadow represents an outline of the complete fingerprint plot.

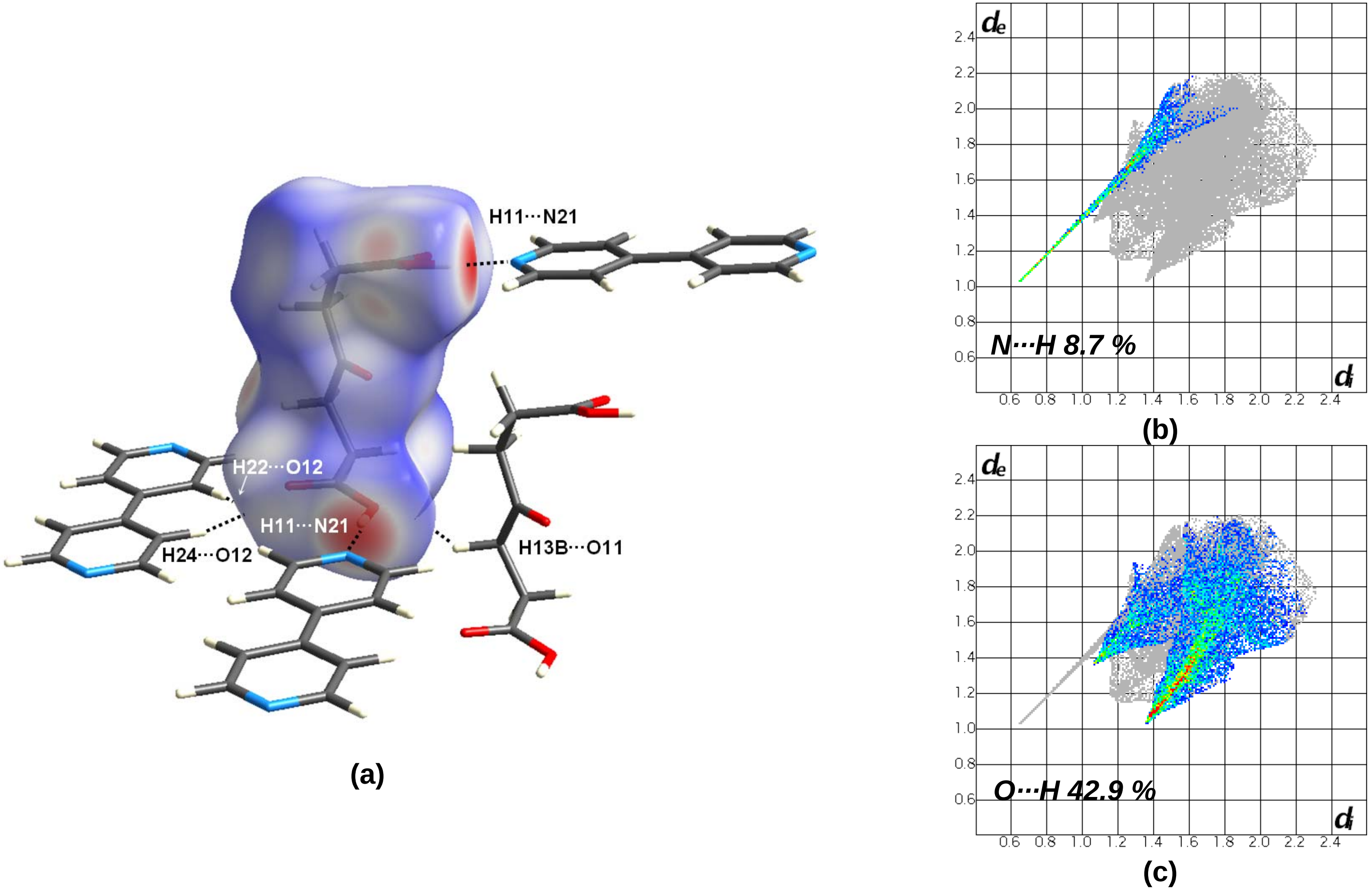
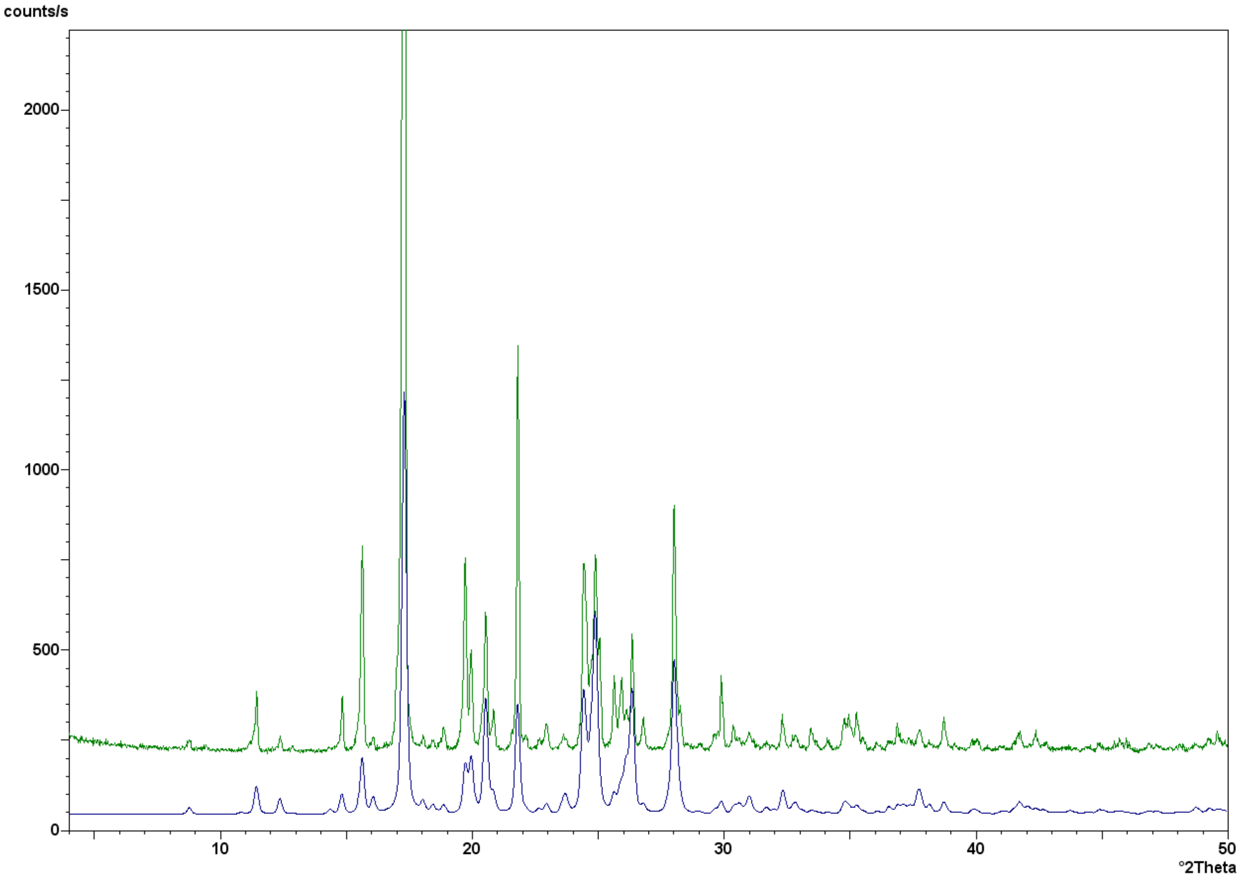


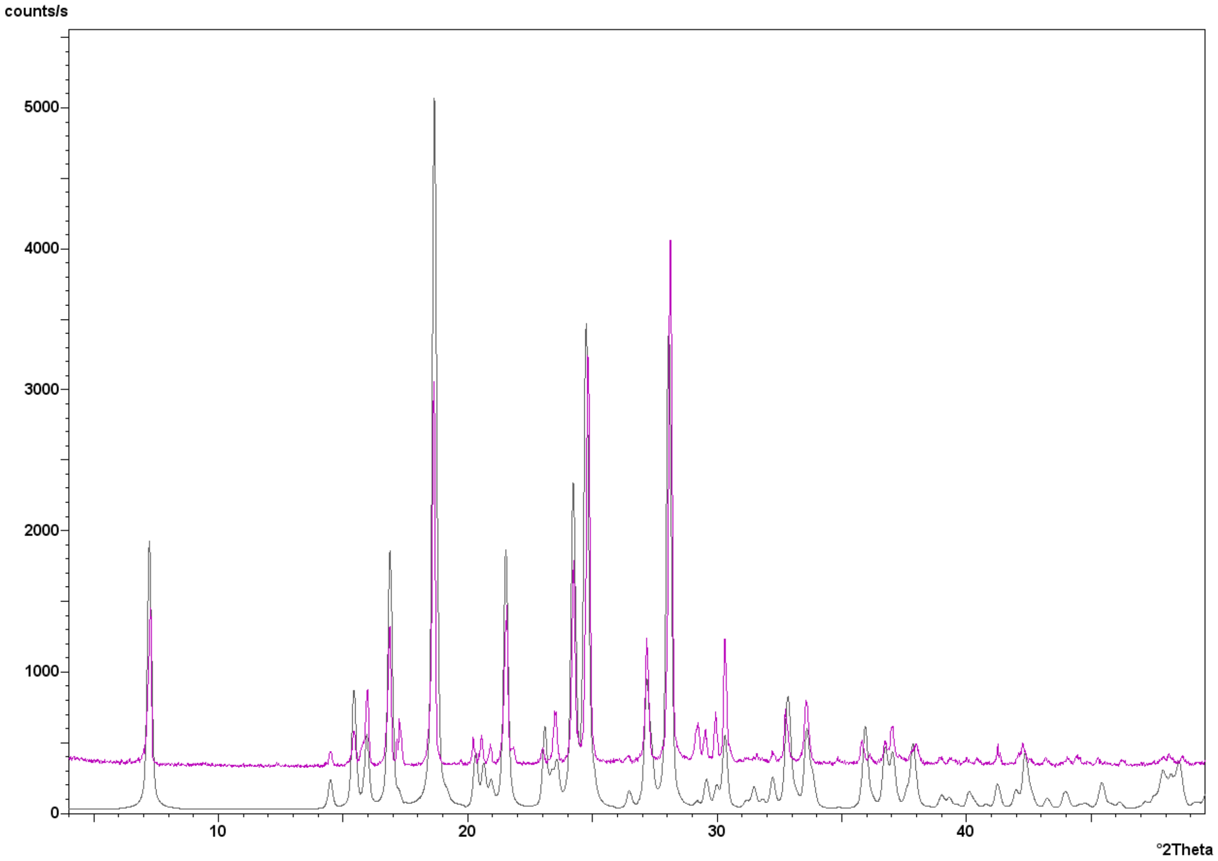
Figure S6. (a) Hirshfeld surface for **opa** in Form II mapped with d_{norm} over the range –0.8 to 1.3. Close contacts with neighbouring molecules are presented with dashed lines;
(b) and (c) fingerprint plots for **opa** in Form II, broken down into contributions from specific pairs of atom-types. The grey

shadow represents an outline of the complete fingerprint plot.

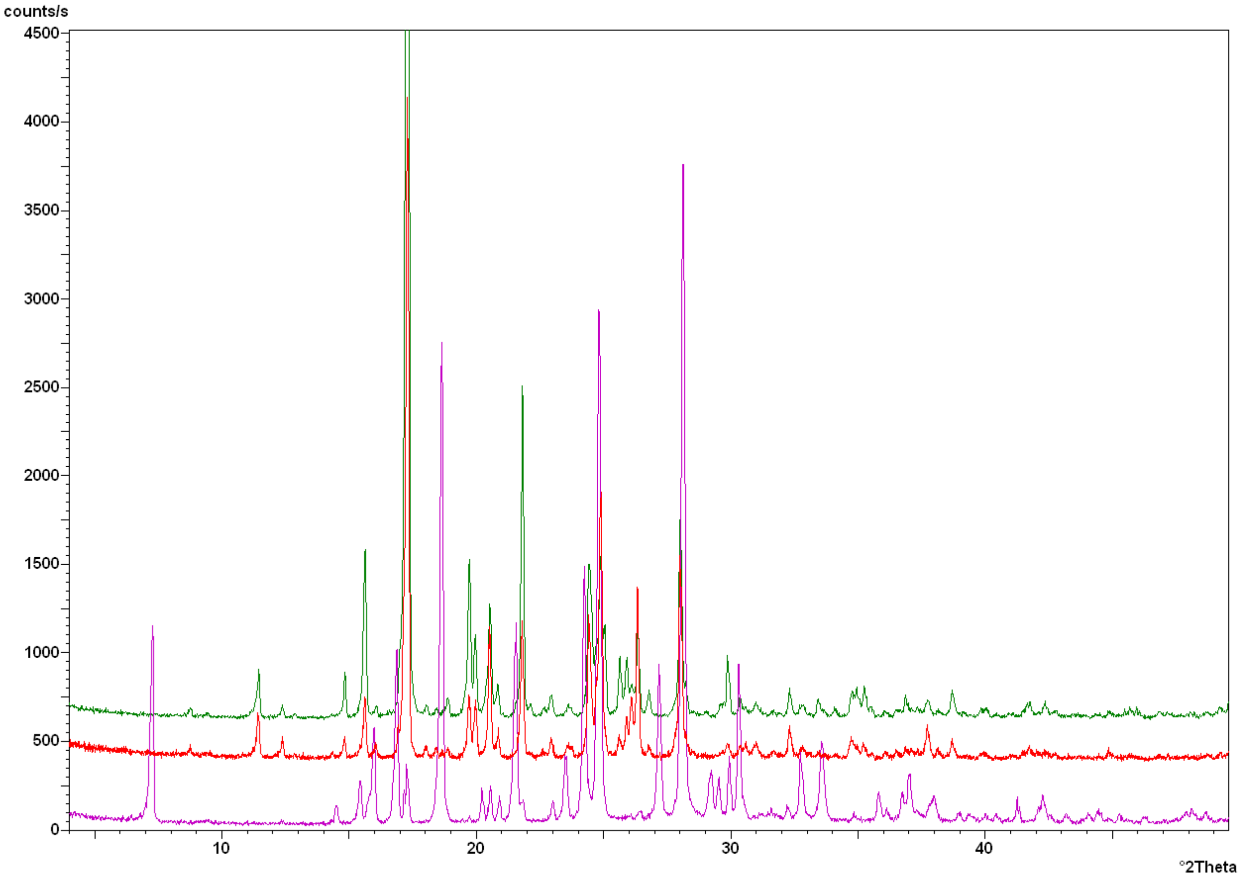
X-ray powder diffraction data



(a)



(b)



(c)

Figure S7. (a) Comparison of powder patterns for Form I (calculated-blue, experimental-green); (b) comparison of powder patterns for Form II (calculated-gray, experimental-magenta); (c) experimental powder patterns of Form II (magenta), product collected after heating of Form II to 100 °C (red) and pattern of Form I (green).

References

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[9] (a) http://hirshfeldsurface.net/CrystalExplorer/index.shtml. (b) McKinnon, J. J., Spackman, M. A., Mitchell, A. S. *Acta Cryst.* 2004, **B60**, 627-668.