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Supporting information for article:

Supramolecular Heterosynthon Assemblies of *ortho*-Phenylenediamine with Substituted Aromatic Carboxylic Acids

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S1. Synthetic details of the salts

S1.1. Synthesis of OPDP:

OPDP was synthesised by taking an equimolar ratio of OPDA (540 mg) in 10 mL of acetonitrile and phthalic acid (840 mg) in 10 mL of methanol and was dissolved separately by small heating till a clear solution was obtained. The reaction mixture was heated further for half an hour at around 40˚C and was allowed to evaporate slowly at room temperature by covering with aluminium foil which was punctured with small holes. Pale-yellow coloured block shaped crystals of OPDP, suitable for single crystal X-ray structure determinations were obtained after 1 week.

Salt OPDP was also prepared by liquid assisted grinding (LAG) of *o*-phenylenediamine (OPDA) (54 mg, 0.5 mmol) and phthalic acid (84 mg, 0.5 mmol) in 1:1 molar ratio with 3 drops of acetonitrile. The mixture was ground for 20 minutes using mortar and pestle and the powdered product was collected for PXRD studies.

S1.2. Synthesis of OPDS:

OPDS was synthesised by taking an equimolar ratio of OPDA (540 mg) in 10 mL of acetonitrile and salicylic acid (840 mg) in 10 mL of methanol and was dissolved separately by small heating till a clear solution was obtained. The reaction mixture was heated further for half an hour at around 40˚C and was allowed to evaporate slowly at room temperature by covering with aluminium foil which was punctured with small holes. Light brown coloured needle shaped crystals of OPDS, suitable for single crystal X-ray structure determinations were obtained after 1 week.

Salt OPDS was also prepared by liquid assisted grinding (LAG) of *o*-phenylenediamine (OPDA) (54 mg, 0.5 mmol) and phthalic acid (84 mg, 0.5 mmol) in 1:1 molar ratio with 3 drops of acetonitrile. The mixture was ground for 20 minutes using mortar and pestle and the powdered product was collected for PXRD studies.

S1.3. Synthesis of OPDPHB:

OPDPHB was synthesised by taking an equimolar ratio of OPDA (540 mg) in 10 mL of acetonitrile and phthalic acid (690 mg) in 10 mL of methanol and was dissolved separately by small heating till a clear solution was obtained. The reaction mixture was heated further for half an hour at around 40˚C and was allowed to evaporate slowly at room temperature by covering with aluminium foil which was punctured with small holes. Light brown coloured block shaped crystals of OPDPHB, suitable for single crystal X-ray structure determinations were obtained after 1 week.

Salt OPDPHB was also prepared by liquid assisted grinding (LAG) of o-phenylenediamine (OPDA) (54 mg, 0.5 mmol) and p-hydroxybenzoic acid (69 mg, 0.5 mmol) in 1:1 molar ratio with 3 drops of

acetonitrile. The mixture was ground for 20 minutes using mortar and pestle and the powdered product was collected for PXRD studies.

S1.4. Synthesis of OPDPNB:

OPDPNB was synthesized by taking an equimolar mixture of *ortho*-phenylenediamine (540 mg) in 10 mL of acetonitrile and p-nitrobenzoic acid (835 mg) in 15 mL of methanol which was dissolved, filtered (noticed that in the methanol the acid was not dissolved completely, but after adding the amine, it results in a clear mixture of both) and allowed to evaporate slowly at room temperature by covering with aluminium foil which was punctured with small holes. Light brown color plate-shaped crystals of OPDPNB suitable for single crystal X-ray structure determination were obtained after one week.

Salt OPDPNB was also prepared by liquid assisted grinding (LAG) of o-phenylenediamine (OPDA) (54 mg, 0.5 mmol) and 4-NBA (83.6 mg, 0.5 mmol) in 1:1 molar ratio with 3 drops of acetonitrile. The mixture was ground for 20 minutes using mortar and pestle and the powdered product was collected for PXRD studies.

Synthesis of OPDDNB:

OPDDNB was synthesized by taking an equimolar mixture of *ortho*-phenylenediamine (108 mg) in 5 mL of acetonitrile and 3,5–dinitrobenzoic acid (212 mg) in 5 mL of methanol which was dissolved, filtered and allowed to evaporate slowly at room temperature by covering with aluminium foil which was punctured with small holes. Yellow colored block shaped crystals of OPDDNB, suitable for single crystal X-ray structure determinations were crystallized after two weeks.

Salt OPDDNB was also prepared by liquid assisted grinding (LAG) of o-phenylenediamine (OPDA) (54 mg, 0.5 mmol) and 3,5-DNBA (106 mg, 0.5 mmol) in 1:1 molar ratio with 3 drops of acetonitrile. The mixture was ground for 20 minutes using mortar and pestle and the powdered product was collected for PXRD studies.

Synthesis of OPDPHB 3P: 120 mg of LAG powder of OPDPHB was dissolved in 15 mL of methanol, gently heated for about 5 minutes with stirring and the solution was then allowed to evaporate slowly at room temperature by covering with aluminium foil which was punctured with small holes. Light brown coloured block shaped crystals of OPDPHB, suitable for single crystal X-ray structure determinations were obtained after 1 week.

Single crystal X-ray diffraction of OPDPHB 3P

Intensity data for OPDPHB (3P) was collected on Rigaku (Xta LAB mini II) diffractometer equipped with air-cooled HPC detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. Data were collected and reduced by using the "CrysAlispro" program (CrysAlisPro, 2015).

An empirical absorption correction using spherical harmonics was implemented in the "SCALE3 ABSPACK" scaling algorithm. Using Olex2 (Dolomanov *et al*., 2009), the structure was solved with the ShelXS (Sheldrick, 2008) structure solution program using Direct Methods and refined with the ShelXL (Sheldrick, 2015) refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Crystal data, data collection and structure refinement details are summarized in Table S1.

Table S1 Experimental details

	(OPDP) 1	(OPDS) 2	(OPDPHB) 3	(OPDPNB) 4
Crystal data				
Chemical formula	$C_6H_9N_2{\cdot}C_8H_5O_4$	$C_7H_5O_3{\cdot}C_6H_9N_2$	$C_6H_9N_2{\cdot}C_7H_6O_3{\cdot}C_6H_8N_2{\cdot}C_7H_5O_3$	$C_6H_9N_2{\cdot}C_7H_4NO_4$
M_r	274.27	246.26	492.52	275.26
Crystal system, space group	Triclinic, *P*-1	Monoclinic, $P2_1/c$	Triclinic, *P*-1	Monoclinic, $P2_1$
Temperature (K)	298	298	298	298
a, *b*, *c* (Å)	4.101 (2), 11.892 (7), 13.092 (8)	4.7832 (7), 11.6783 (17), 21.859 (3)	9.9374 (5), 14.3212 (6), 18.2929 (11)	8.881 (2), 6.0754 (16), 11.995 (3)
α, β, γ (°)	93.491 (9), 97.769 (10), 90.28 (1)	90, 93.999 (2), 90	72.196 (4), 81.185 (5), 82.068 (4)	90, 91.021 (4), 90
V (Å^3)	631.4 (6)	1218.1 (3)	2437.9 (2)	647.1 (3)
Z	2	4	4	2
Radiation type	Mo *K*α	Mo *K*α	Cu *K*α	Mo *K*α
μ (mm^{-1})	0.11	0.10	0.80	0.11
Crystal size (mm)	0.34 × 0.28 × 0.22	0.42 × 0.36 × 0.32	0.32 × 0.28 × 0.22	0.38 × 0.12 × 0.09
Data collection				

Diffractometer	Bruker Apex CCD area detector	Bruker Apex CCD area detector	Xcalibur, Eos, Gemini	Bruker Apex CCD area detector
Absorption correction	Multi-scan *SADABS*	Multi-scan *SADABS*	Multi-scan *CrysAlis PRO*	Multi-scan *SADABS*
T_{min}, T_{max}	0.977, 0.964	0.867, 0.876	0.301, 1.000	0.960, 0.990
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6461, 2454, 2083	13780, 2926, 2396	15886, 9322, 7257	2914, 2026, 1635
R_{int}	0.022	0.035	0.023	0.018
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.667	0.618	0.594
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.122, 1.05	0.049, 0.131, 1.08	0.048, 0.135, 1.04	0.050, 0.126, 1.04
No. of reflections	2454	2926	9322	2026
No. of parameters	205	188	690	201
No. of restraints	2	0	0	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.18	0.24, −0.22	0.20, −0.29	0.16, −0.16

Absolute structure	NA	NA	NA	Flack x determined using 533 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61).
Absolute structure parameter	NA	NA	NA	0.2 (10)

	(OPDDNB) 5	(OPDPHB) 3P
Crystal data		
Chemical formula	$C_6H_9N_2 \cdot C_7H_3N_2O_6$	$C_6H_9N_2 \cdot C_7H_6O_3 \cdot C_6H_8N_2$
M_r	320.27	354.40
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1$
Temperature (K)	298	298
a, *b*, *c* (Å)	11.9565 (10), 5.7973 (5), 20.2355 (16)	8.628(2), 5.7938(16), 18.172(4)
α, β, γ (°)	90, 96.805 (1), 90	90, 90.69(2), 90
V (Å^3)	1392.8 (2)	908.3(4)
Z	4	2
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.12	0.090
Crystal size (mm)	0.4 × 0.32 × 0.22	0.21 × 0.18 × 0.08
Data collection		
Diffractometer	CCD area detector	Xta LAB Mini II
Absorption correction	Multi-scan *SADABS*	Multi-scan *CrysAlis PRO* 1.171.39.20a

T_{min}, T_{max}	0.952, 0.973	0.749, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8392, 2720, 2255	3528, 2044, 1811
R_{int}	0.022	0.040
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617	0.556
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.103, 1.03	0.045, 0.143, 1.11
No. of reflections	2720	2044
No. of parameters	229	266
No. of restraints	1	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.22	0.22, -0.21
Absolute structure	NA	Flack x determined using 548 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61).
Absolute structure parameter	NA	−0.6 (10)

Computer programs: Bruker *SMART*, *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35h (release 09-02-2015 CrysAlis171 .NET) (compiled Feb 9 2015, 16:26:32), *SAINT* v6.45A (Bruker, 2003), Bruker *SAINT*, *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), Olex2 (Dolomanov *et al.*, 2009).

Table S2 Hydrogen-bond geometry (Å, º) for (OPDPHB 3P)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*C*···N4^{i}	0.82	2.00	2.807 (6)	166
N3—H3*B*···O3^{ii}	0.87	2.62	3.421 (5)	154
N1—H1*A*···O1^{i}	0.81 (6)	1.92 (6)	2.713 (6)	165

N1—H1*B*···O2^{ii}	1.11 (6)	1.74 (7)	2.821 (5)	164
N1—H1*C*···O2	1.04 (6)	1.67 (6)	2.688 (5)	165
N2—H2*A*···O1	1.02 (8)	2.33 (7)	3.203 (7)	143
N4—H4*A*···O3^{iii}	0.83 (5)	2.28 (5)	3.060 (6)	157

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1; (ii) −*x*+1, *y*−1/2, −*z*+1; (iii) *x*, *y*, *z*−1.

Table S3 Important bond lengths and angles of salts 1-5 along with the polymorph (OPDPHB 3P)

Atom 1	Atom 2	**Bond length/ Å**
OPDP		
C13	O1	1.233(2)
C13	O2	1.263(2)
C14	O3	1.224(2)
C14	O4	1.279(2)
C1	N1	1.461 (2)
C2	N2	1.378(2)
OPDS		
C13	O1	1.2527(16)
C13	O2	1.2693(16)
C1	N1	1.4627(16)
C2	N2	1.3951(19)
OPDPHB		
C1A	N1A	1.464(2)
C2A	N2A	1.404(2)
C1B	N1B	1.456(2)
C2B	N2B	1.410(2)
C1C	N1C	1.413(2)
C2C	N2C	1.415(2)
C1D	N1D	1.423(2)
C2D	N2D	1.413(2)
C10A	O3A	1.362(2)
C1OC	O3C	1.3647(19)
C10D	O3D	1.363(2)
C13A	O1A	1.211(2)
C13A	O2A	1.309(2)
C13B	O1B	1.247(2)
C13B	O2B	1.270(2)

Atom 1	**Atom 2**	**Atom 3**	**Bond angle/ º**
OPDP			
C2	C1	N1	118.96(15)
C6	C1	N1	119.39(14)
N2	C2	C1	121.59(15)
N2	C2	C3	121.12(16)
O1	C13	C7	119.03(14)
O1	C13	O2	121.09(16)
O2	C13	C7	119.88(14)
O3	C14	C8	119.00(15)
O3	C14	O4	119.34(15)
O4	C14	C8	121.65(14)
OPDS			
O3	C8	C7	121.63(13)
O3	C8	C9	118.38(15)
O1	C13	O2	122.62(12)
O1	C13	C7	119.52(11)
O2	C13	C7	117.85(12)
C2	C1	N1	118.70(11)
C3	C2	N2	122.04(13)
OPDPHB			
C2A	C1A	N1A	120.87(15)
C6A	C1A	N1A	117.23(17)
C1A	C2A	N2A	122.58(16)
C3A	C2A	N2A	119.73(18)
C2B	C1B	N1B	119.18(16)
C6B	C1B	N1B	119.80(18)
C1B	C2B	N2B	120.93(17)
C3B	C2B	N2B	121.66(19)
O3A	C10A	C9A	117.99(16)
O3A	C10A	C11A	122.35(17)
O1A	C13A	C7A	122.69(17)
O1A	C13A	O2A	121.69(17)

C13C	O1C	1.245(2)
C13C	O2C	1.265(2)
C13D	O1D	1.221(2)
C13D	O2D	1.299(2)
OPDPNB		
C1	N1	1.466(5)
C2	N2	1.391(6)
C10	N3	1.473(6)
C13	O1	1.252(5)
C13	O2	1.259(5)
N3	O3	1.202(7)
N3	O4	1.203(6)
OPDDNB		
C1	N1	1.4645(18)
C2	N2	1.414(2)
C9	N3	1.4668(18)
C11	N4	1.4689(19)
C13	O1	1.2364(18)
C13	O2	1.2488(17)
N3	O3	1.2182(18)
N3	O4	1.2231(17)
N4	O5	1.2160(17)
N4	O6	1.2228(18)
OPDDNB 3P		
C1	N1	1.462(6)
C2	N2	1.392(6)
C7	N3	1.397(6)
C8	N4	1.412(6)
C19	O1	1.227(6)
C19	O2	1.269(5)
C16	O3	1.374(5)

O2A	C13A	C7A	115.62(15)
C2C	C1C	N1C	120.30(17)
C6C	C1C	N1C	119.89(19)
C1C	C2C	N2C	119.85(17)
C3C	C2C	N2C	121.87(19)
C2D	C1D	N1D	120.54(17)
C6D	C1D	N1D	120.25(18)
C1D	C2D	N2D	119.88(16)
C3D	C2D	N2D	120.92(18)
O3D	C10D	C9D	117.85(16)
O3D	C10D	C11D	122.47(17)
O1D	C13D	C7D	121.39(18)
O1D	C13D	O2D	123.43(18)
O2D	C13D	C7D	115.18(16)
O3C	C10C	C9C	117.76(15)
O3C	C10C	C11C	122.55(16)
O1C	C13C	C7C	117.09(16)
O1C	C13C	O2C	123.80(16)
O2C	C13C	C7C	119.08(15)
O3B	C10B	C9B	122.67(18)
O3B	C10B	C11B	117.72(17)
O1B	C13B	C7B	118.82(18)
O1B	C13B	O2B	123.85(18)
O2B	C13B	C7B	117.33(16)
OPDPNB			
C2	C1	N1	117.9(3)
C6	C1	N1	120.4(4)
C3	C2	N2	121.7(4)
N2	C2	C1	121.6(4)
C9	C10	N3	119.0(5)
C11	C10	N3	118.5(5)
O1	C13	C7	117.6(4)
O1	C13	O2	124.7(4)
O2	C13	C7	117.7(4)
O3	N3	C10	118.5(6)
O3	N3	O4	122.8(5)
O4	N3	C10	118.6(5)
OPDDNB			
C2	C1	N1	118.94(13)
C6	C1	N1	119.34(13)
C1	C2	N2	119.97(13)
C3	C2	N2	122.45(14)
C8	C9	N3	118.57(13)
C10	C9	N3	118.09(13)

C10	C11	N4	118.14(13)
C12	C11	N4	119.12(13)
O1	C13	C7	117.17(13)
O1	C13	O2	125.65(14)
O2	C13	C7	117.18(13)
O3	N3	C9	117.99(13)
O3	N3	O4	123.65(13)
O4	N3	C9	118.36(13)
O5	N4	C11	118.36(14)
O5	N4	O6	123.86(13)
O6	N4	C11	117.78(13)
OPDDNB 3P			
C1	C2	N2	120.7(4)
C2	C1	N1	118.5(4)
C6	C1	N1	119.2(4)
C7	C8	N4	119.0(4)
C8	C7	N3	118.3(4)
C9	C8	N4	121.5(4)
C12	C7	N3	122.8(4)
C15	C16	O3	118.0(4)
N2	C2	C3	121.5(4)
O1	C19	O2	124.0(4)
O1	C19	C13	119.1(5)
O2	C19	C13	117.0(4)
O3	C16	C17	121.0(4)

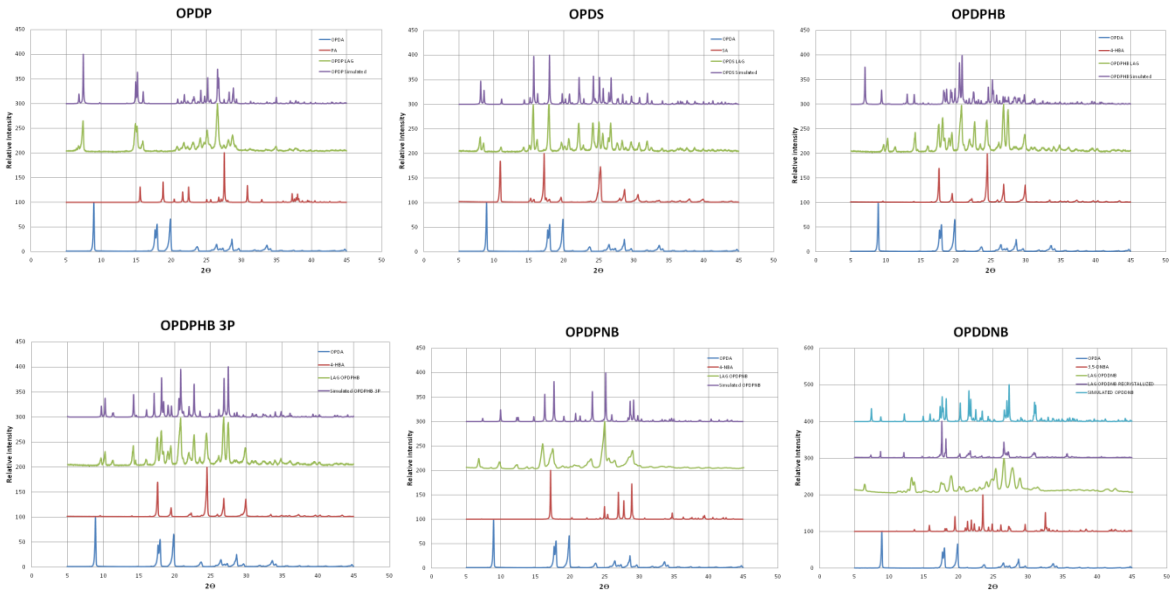

Figure S1 PXRD patterns drawn from the results obtained by 1:1 LAG experiment of the respective salts along with Computed patterns of the respective CIF file.

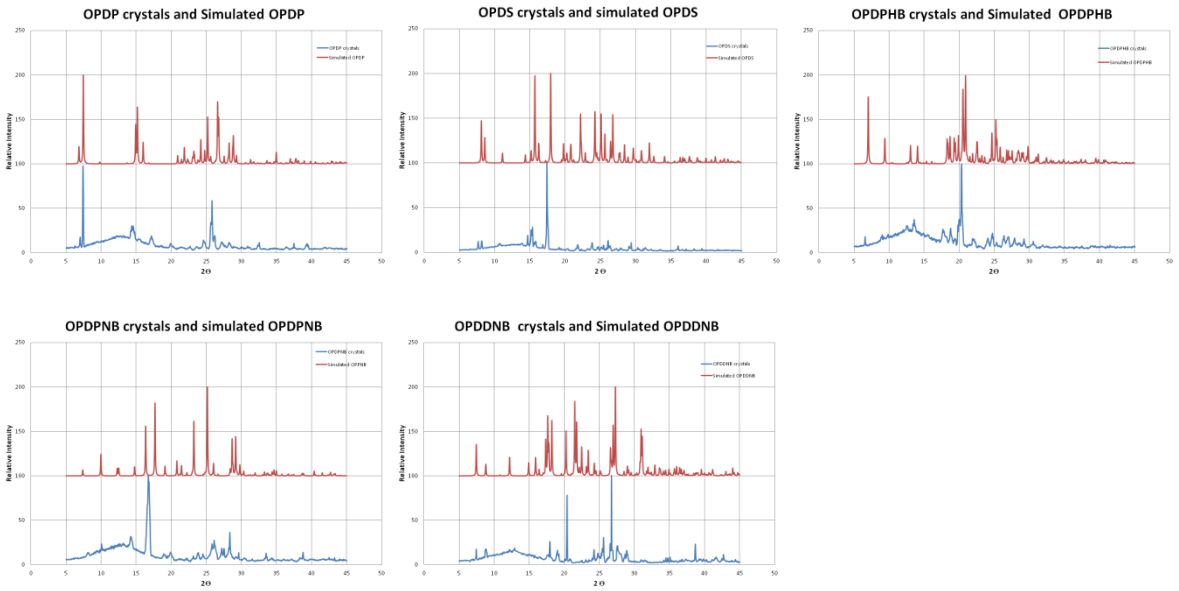

Figure S2 Comparative PXRD patterns drawn from the ground crystals of the respective salts and Computed patterns of the respective CIF file.

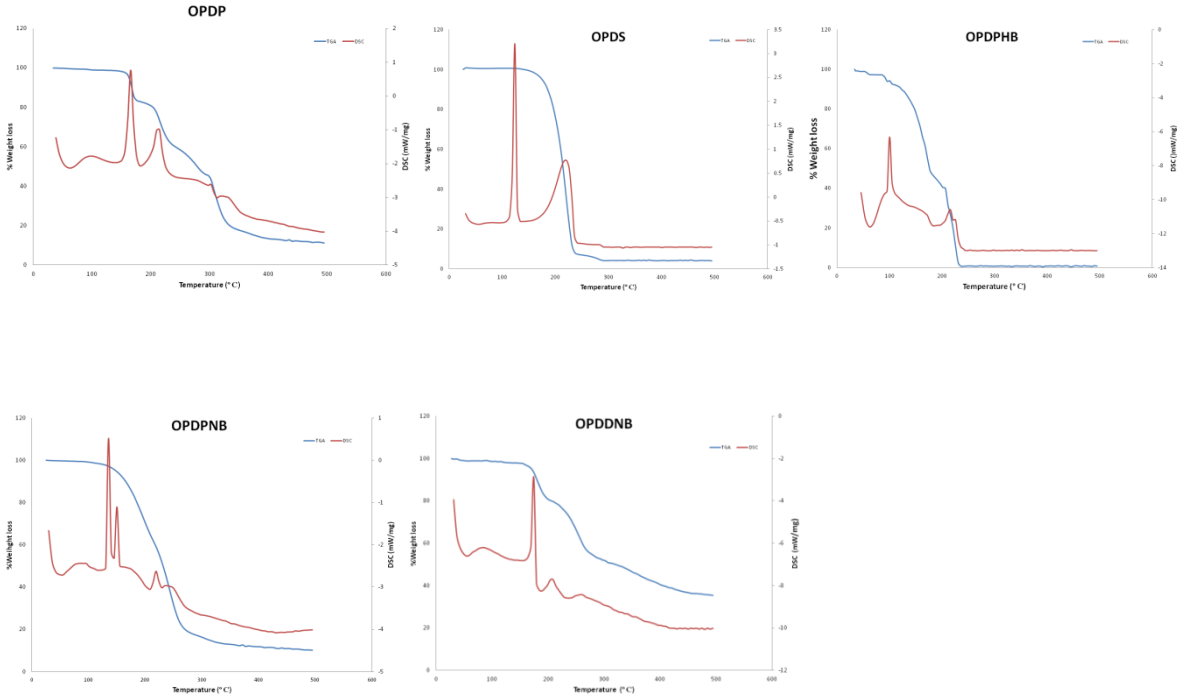

Figure S3 DSC and TGA curve of salts 1-5.

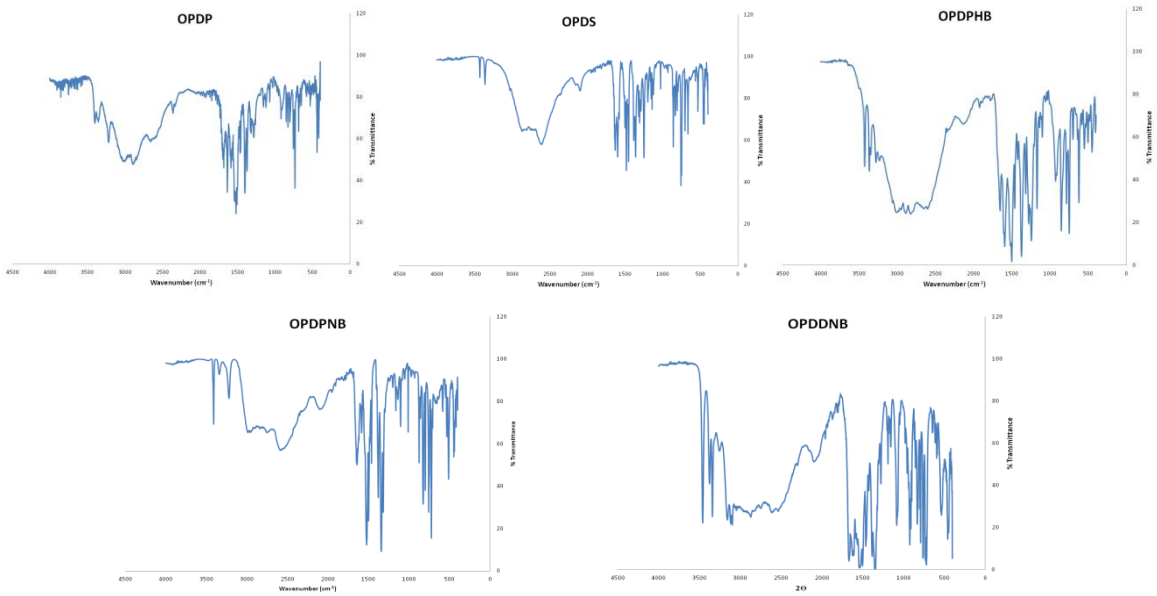

Figure S4 FTIR spectrum of salts 1-5.

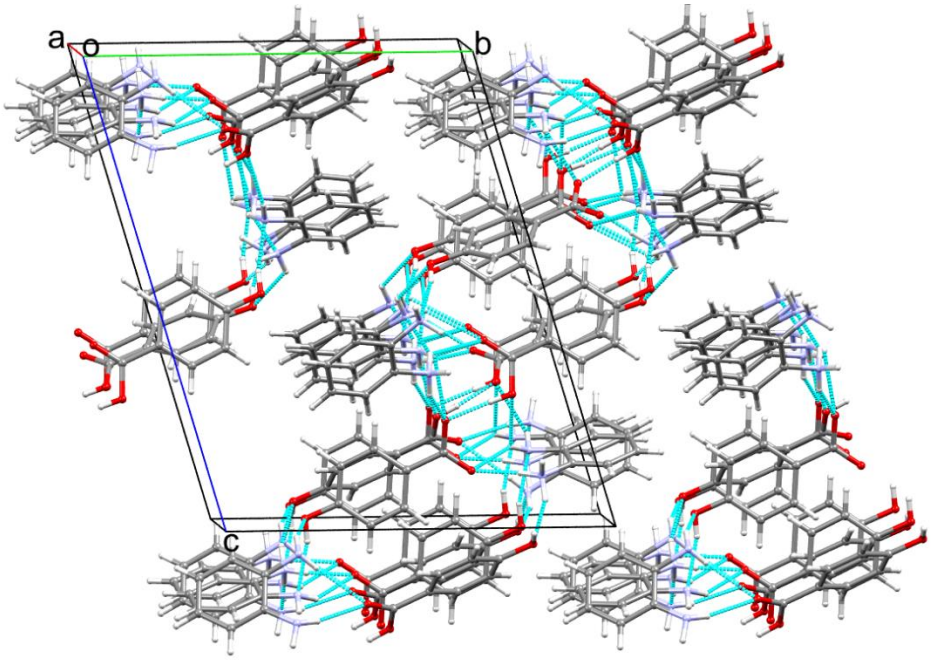

Figure S5 2D supramolecular network of OPDPHB, showing along crystallographic *bc* plane using two types of N–H···O interactions.

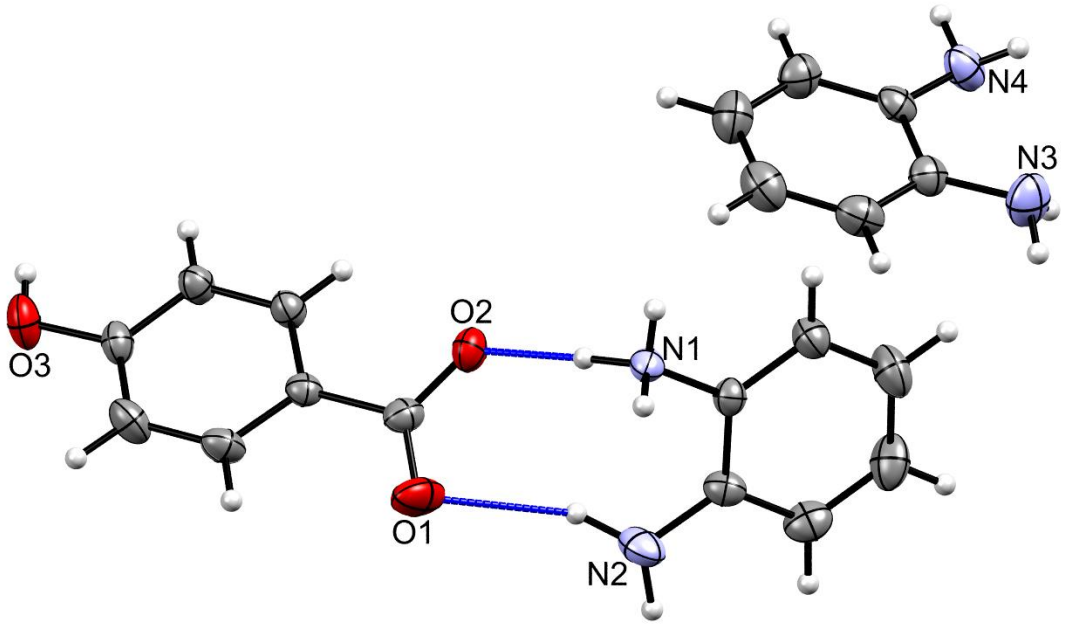

Figure S6 The asymmetric unit of OPDPHB 3P with atom numbering scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius.

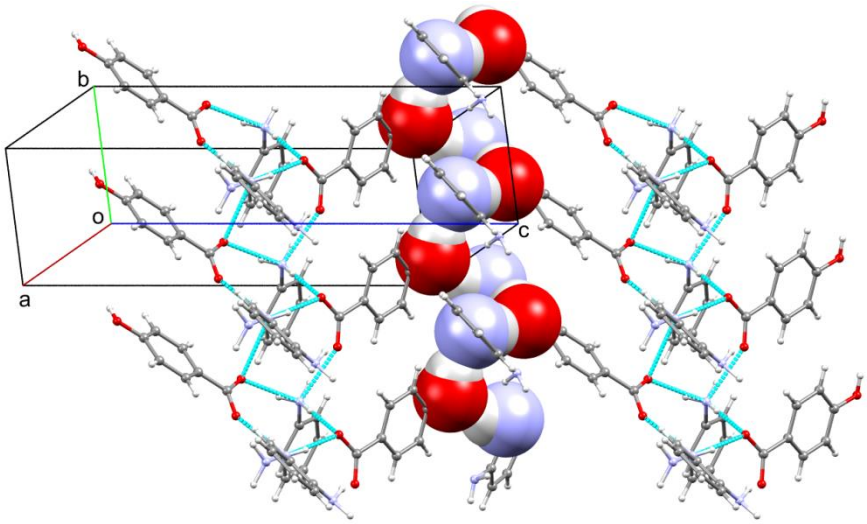

Figure S7 Formation of ladder network assisted by $R_4^3(10)$ heterosynthons along with right handed helices exists alternatively which runs along crystallographic b axis

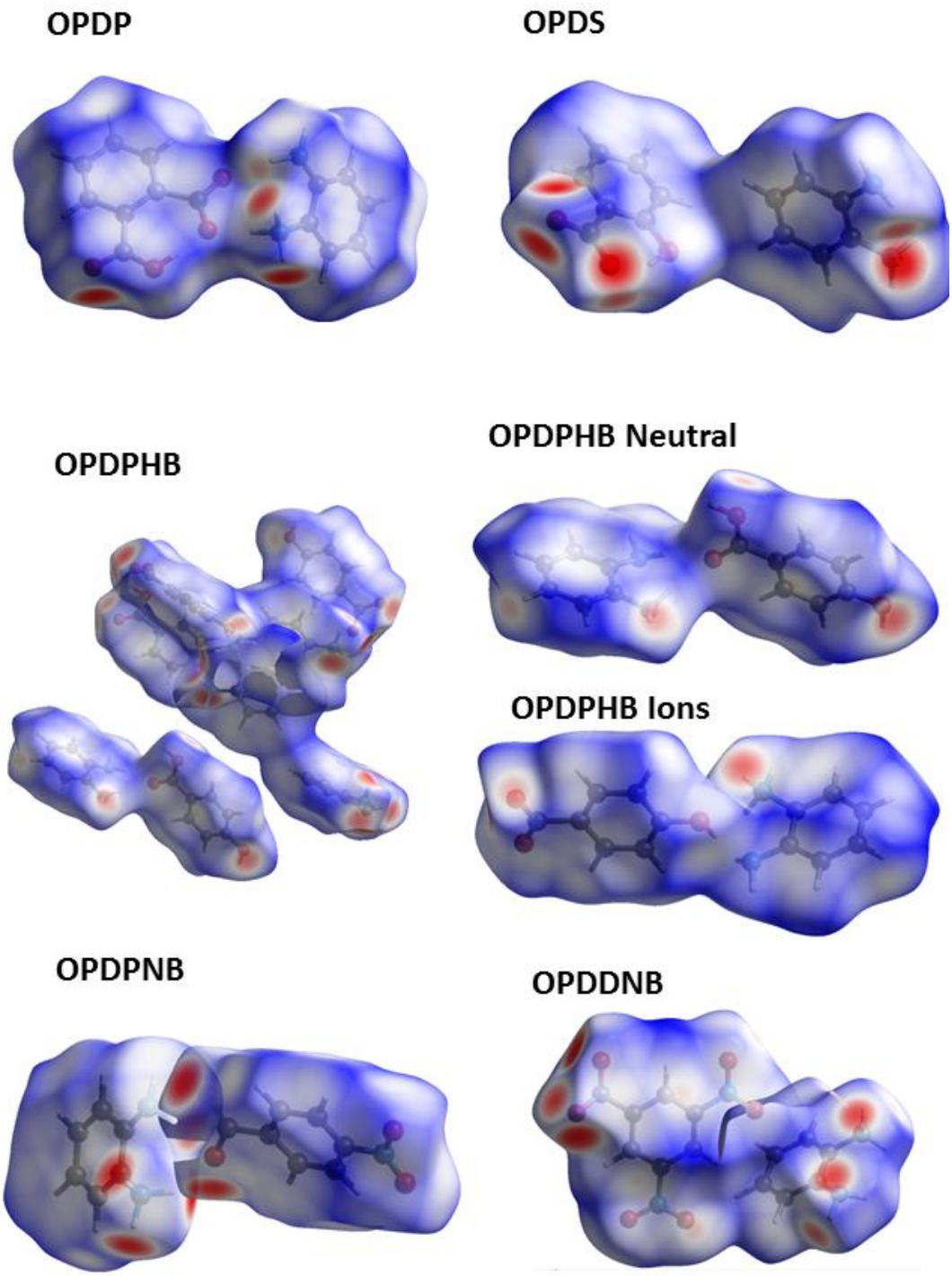

Figure S8 Hirshfeld surfaces mapped with d_{norm} ranging from -0.5 (red) to 1.5 Å (blue).