STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 76 (2020)

Supporting information for article:

Supramolecular cocrystals of O-H···O hydrogen bonded 18-crown-6 with isophthalic acid derivatives: Hirshfeld surface analysis and third-order nonlinear optical properties

C BALAKRISHNAN, M MANONMANI, S RAFI AHAMED, G VINITHA, SP MEENAKSHISUNDARAM and RM SOCKALINGAM

Supporting information

Supplementary Figures

Supplementary Tables

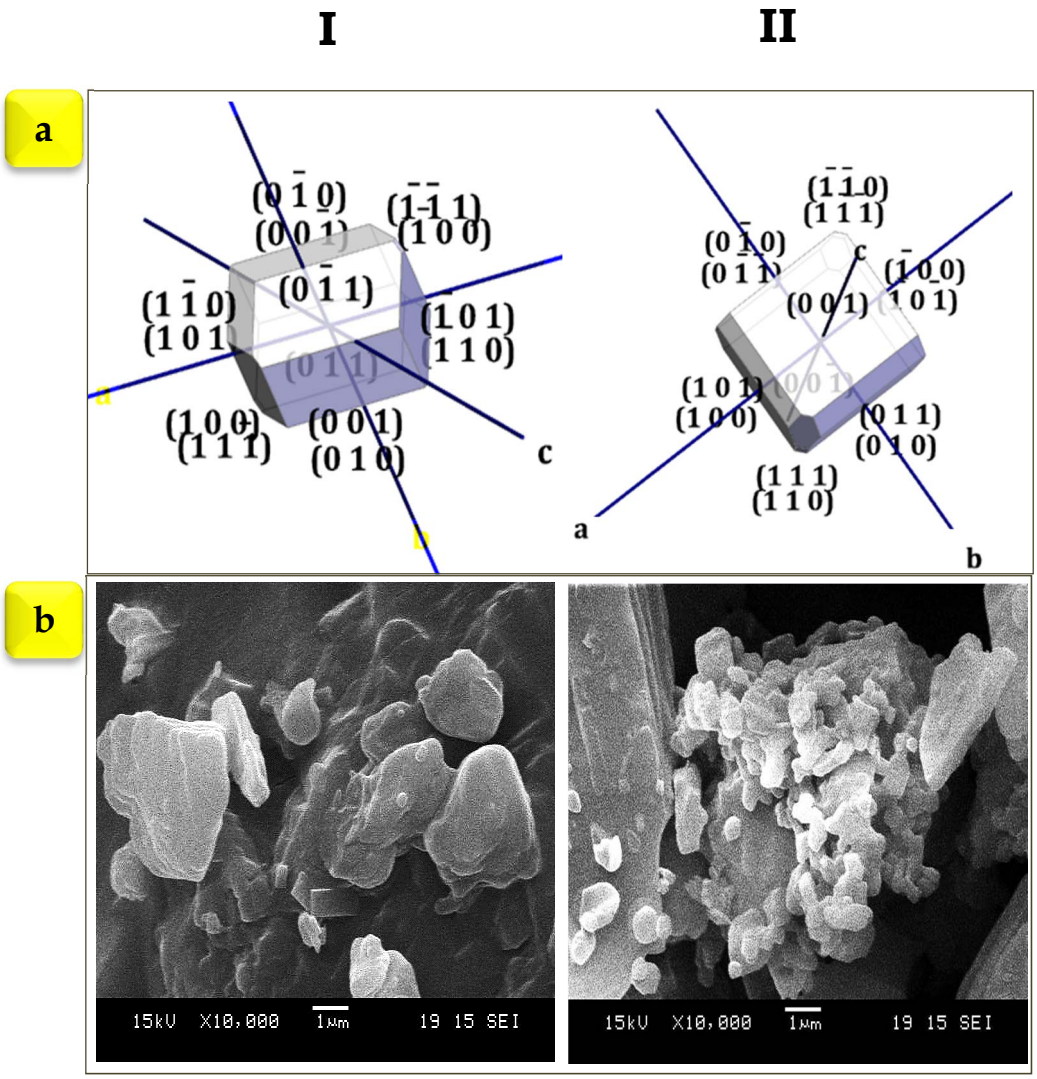

Figure S1 (*a*) Crystal morphology and (*b*) SEM images of **I** and **II** (high surface roughness with scattered defect centers)

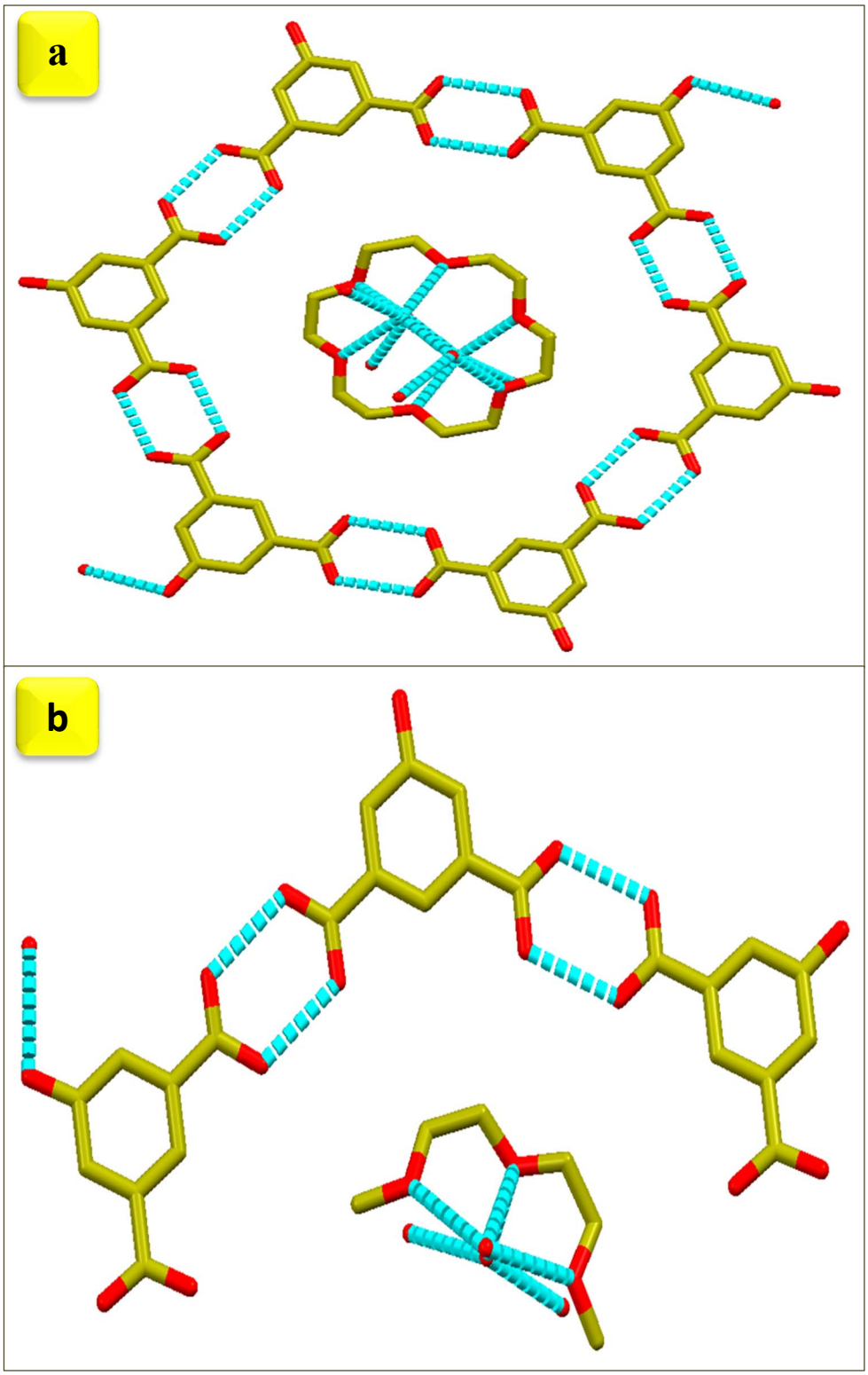

Figure S2 (*a*) The basic unit and (*b*) asymmetric unit of **I**. (all the hydrogen atoms are omitted for clarity and hydrogen bonds are shown in blue dashed line).

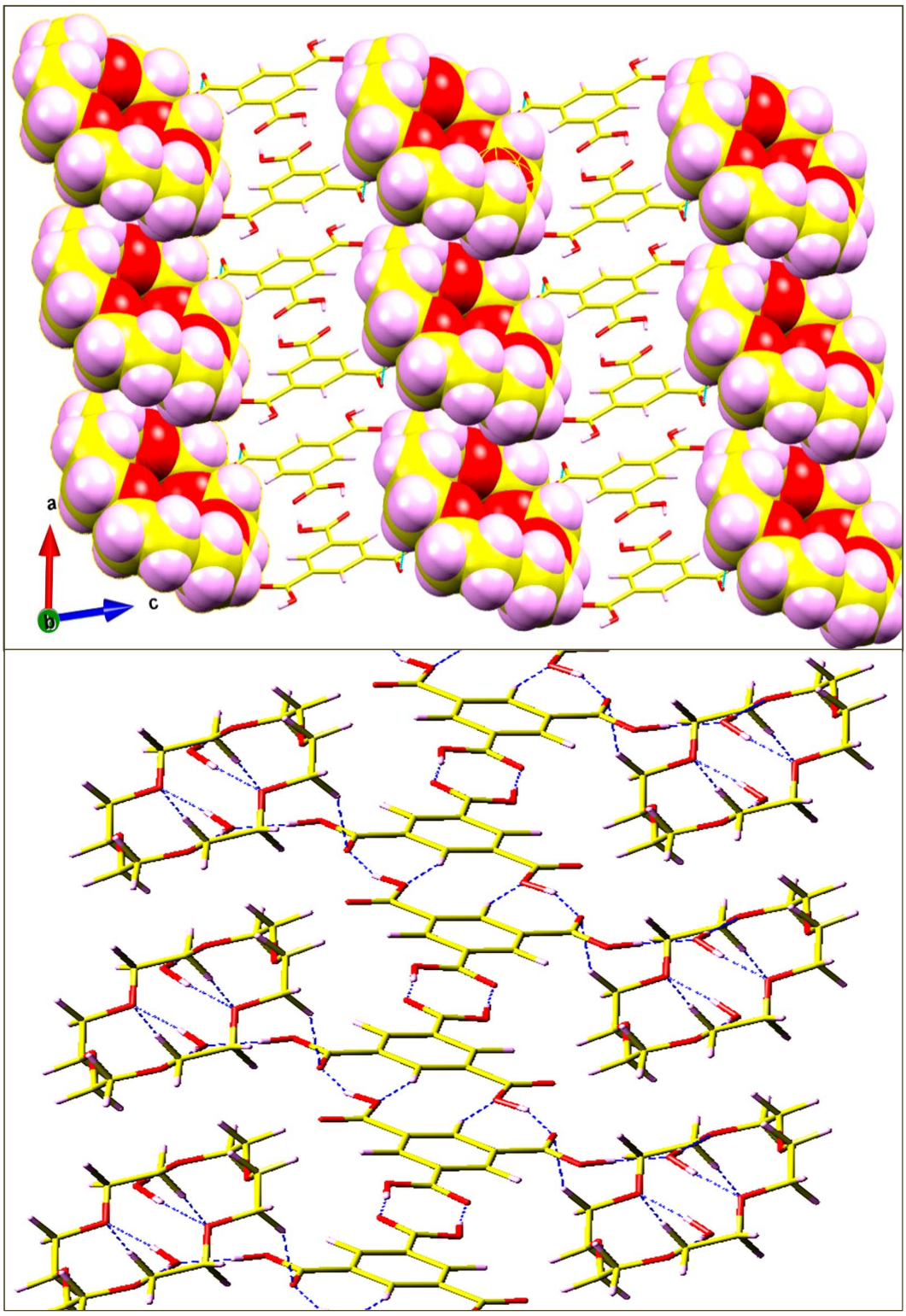

Figure S3 Linking of the hydrogen bonded column-like structure along the b-axis for **II** (space-filling and capped stick representation)

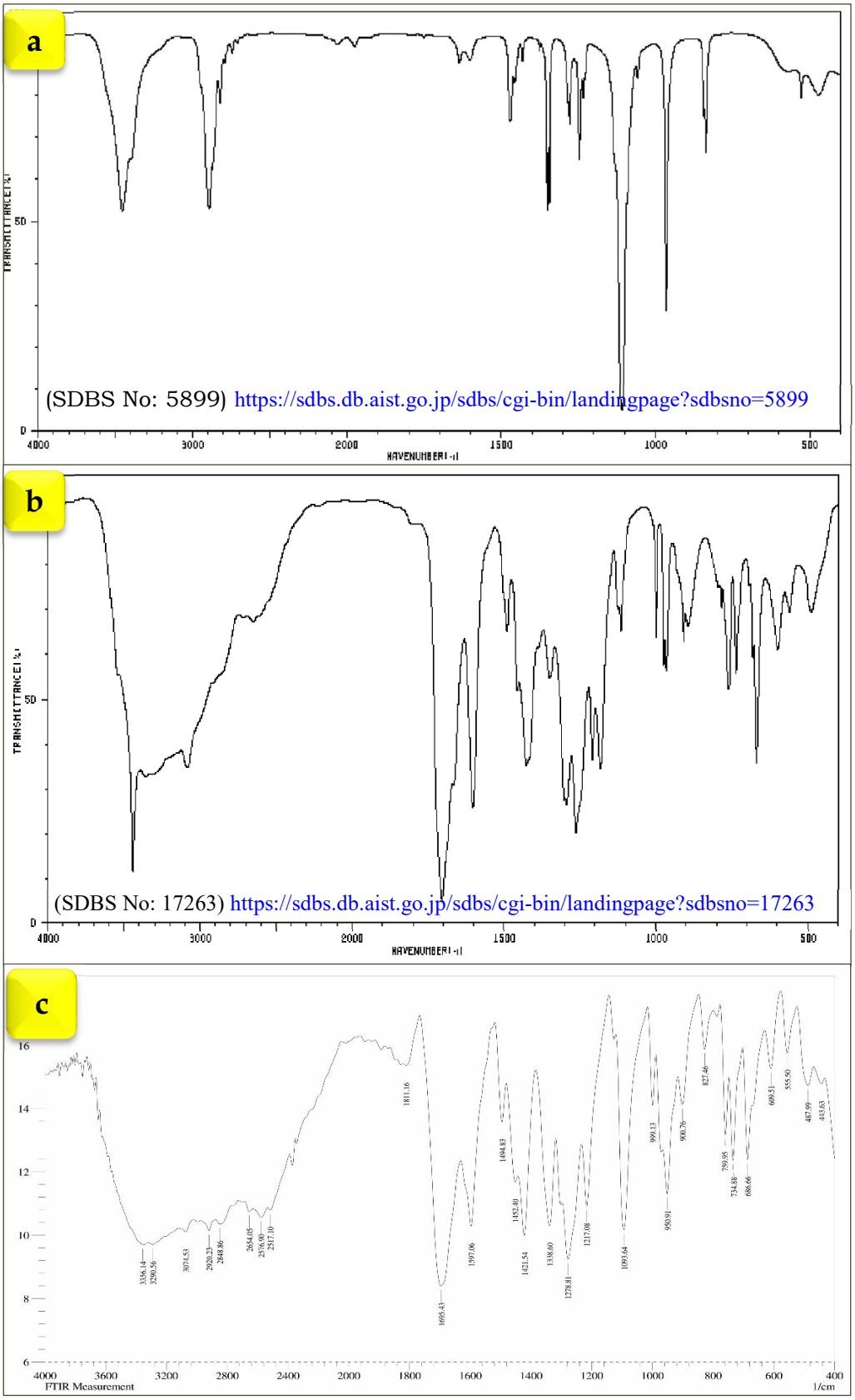

Figure S4 FT-IR spectra of (*a*) 18-crown-6 (*b*) 5HIPA and (*c*) **I**

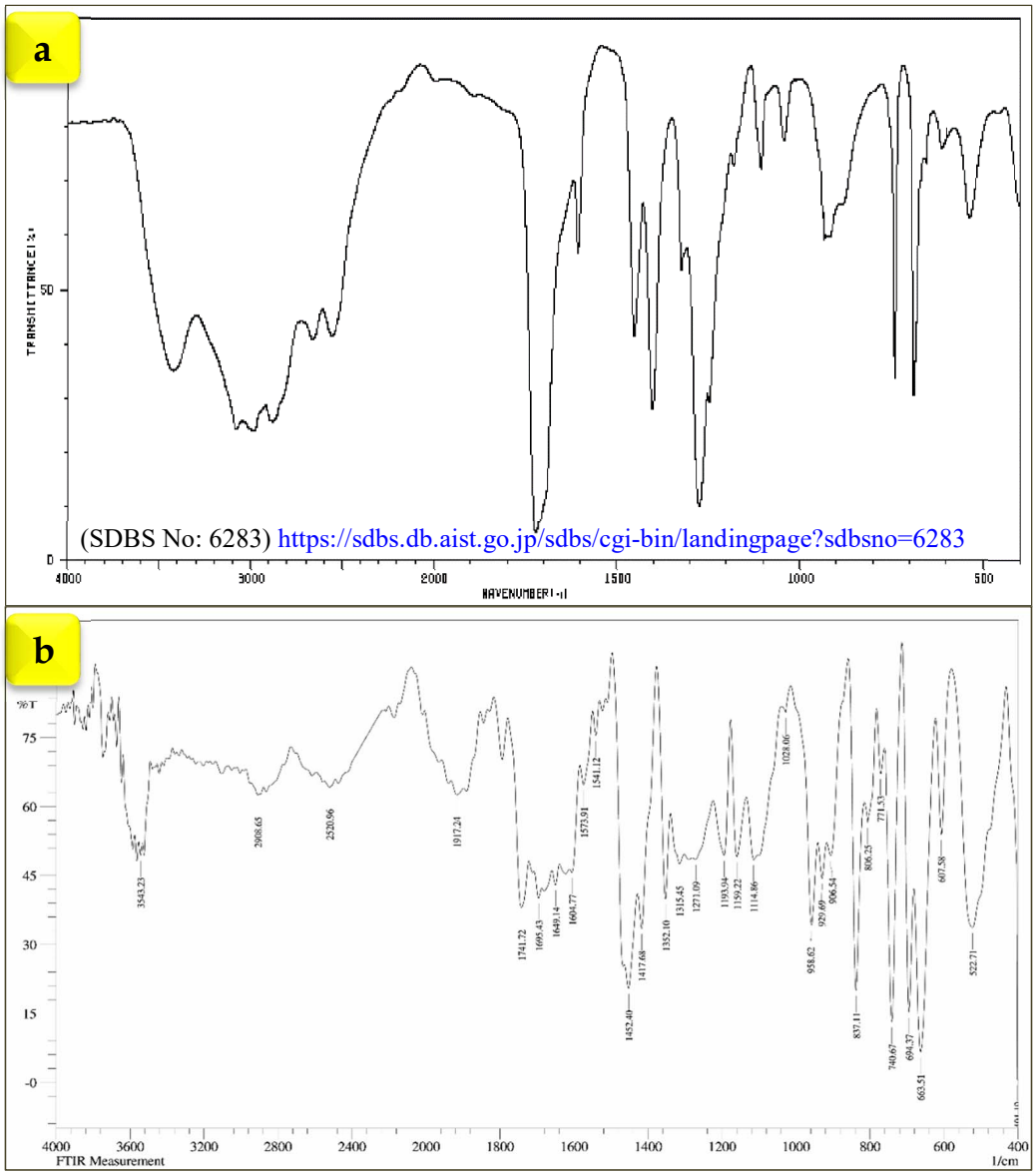

Figure S5 FT-IR spectra of (*a*) TMA and (*b*) **II**

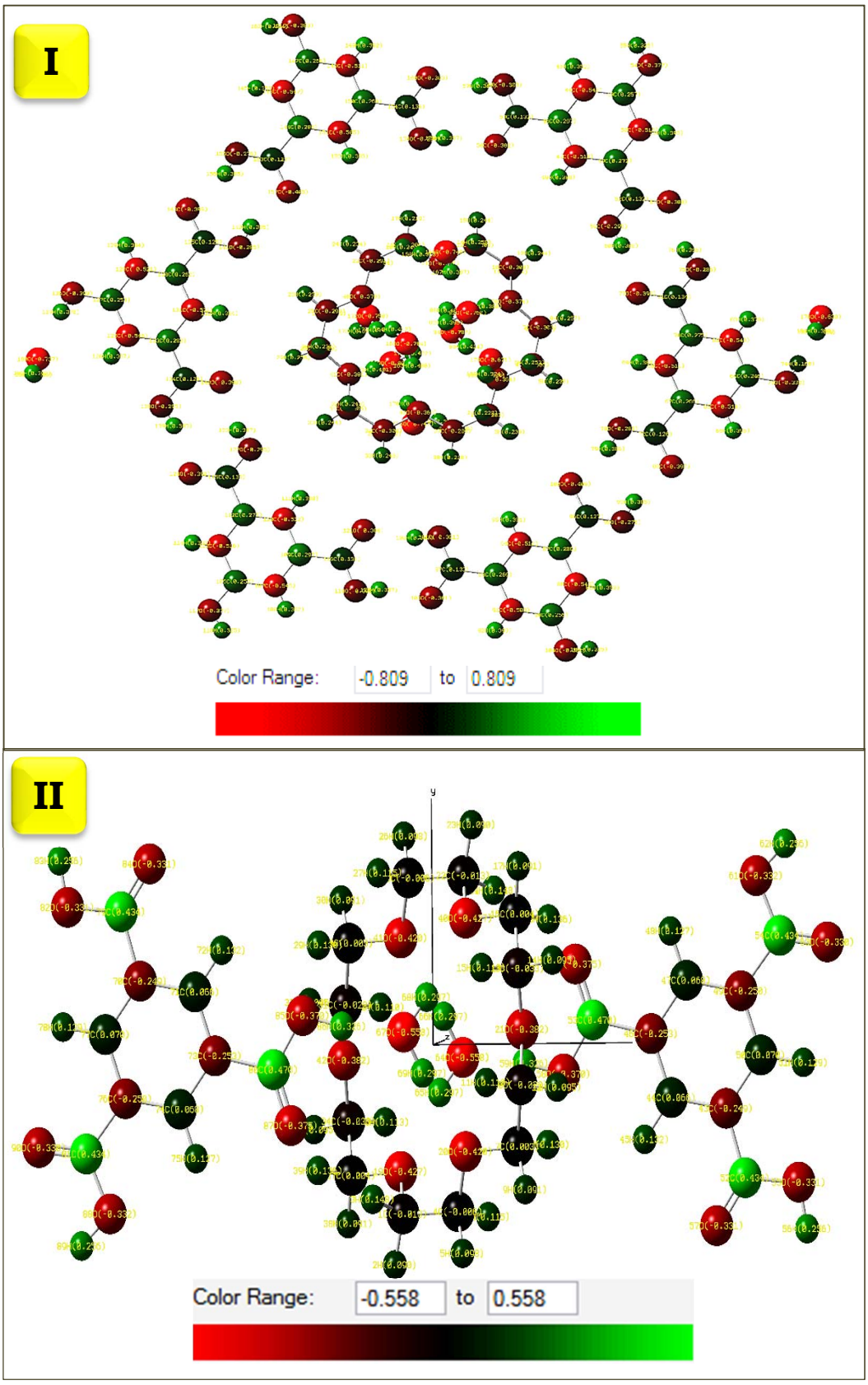

Figure S6 Mulliken atomic charge distribution

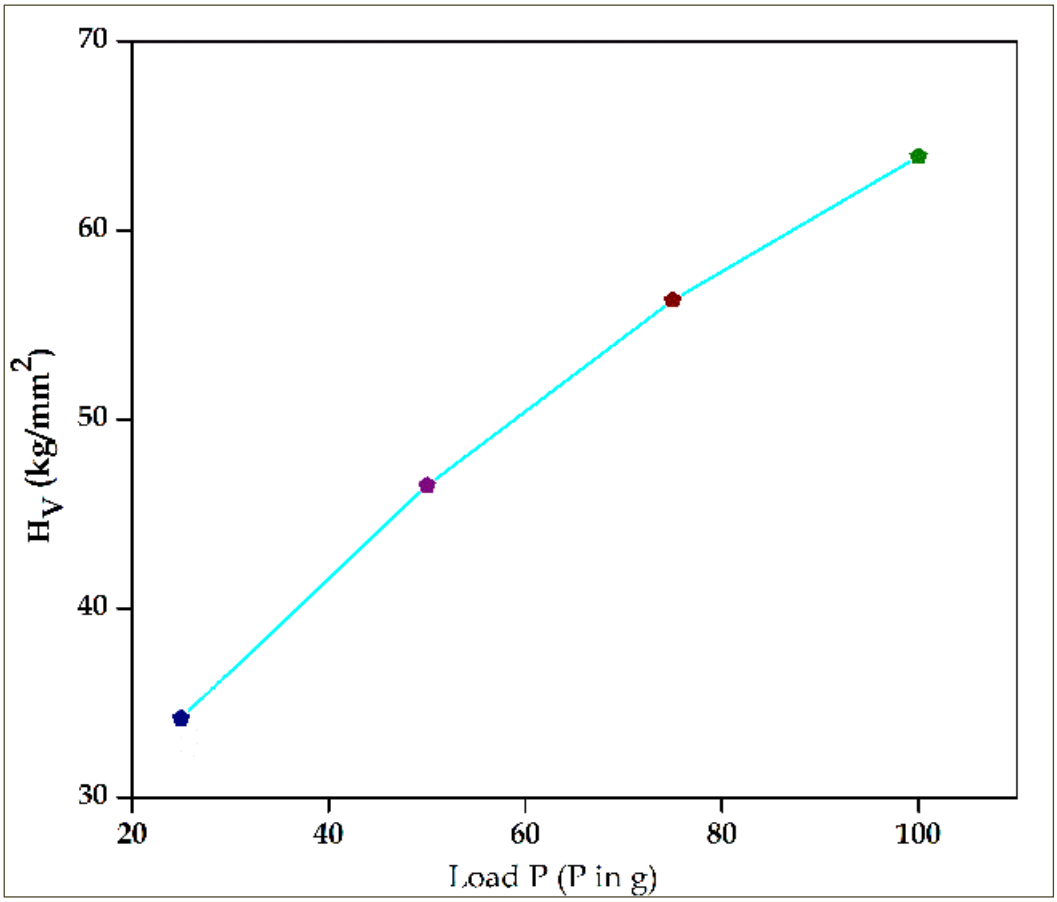

Figure S7 Variation of Hv with applied load P for **II**

Table S1a Bond lengths [Å] for **I**

C(1)-O(1)	1.418(3)	C(11)-C(13)	1.484(3)	C(27)-C(30)	1.488(3)
C(1)-C(6)#1	1.490(5)	C(12)-H(12)	0.93	C(28)-H(28)	0.93
C(1)-H(1A)	0.97	C(13)-O(7)	1.256(2)	C(29)-O(14)	1.243(2)
C(1)-H(1B)	0.97	C(13)-O(8)	1.271(2)	C(29)-O(15)	1.288(2)
C(2)-O(1)	1.425(3)	C(14)-O(6)	1.261(2)	C(30)-O(16)	1.265(2)
C(2)-C(3)	1.486(5)	C(14)-O(5)	1.269(2)	C(30)-O(17)	1.265(2)
C(2)-H(2A)	0.97	C(15)-C(20)	1.387(3)	O(4)-H(4C)	0.82
C(2)-H(2B)	0.97	C(15)-C(16)	1.389(3)	O(5)-H(5C)	0.82
C(3)-O(2)	1.434(3)	C(15)-H(15)	0.93	O(6)-H(6C)	0.82
C(3)-H(3A)	0.97	C(16)-O(9)	1.365(2)	O(7)-H(7A)	0.82
C(3)-H(3B)	0.97	C(16)-C(17)	1.382(3)	O(8)-H(8A)	0.82
C(4)-O(2)	1.413(3)	C(17)-C(18)	1.393(3)	O(9)-H(9C)	0.82
C(4)-C(5)	1.497(5)	C(17)-H(17)	0.93	O(10)-H(10A)	0.82
C(4)-H(4A)	0.97	C(18)-C(19)	1.391(3)	O(11)-H(11A)	0.82
C(4)-H(4B)	0.97	C(18)-C(22)	1.480(3)	O(12)-H(12A)	0.82
C(5)-O(3)	1.433(3)	C(19)-C(20)	1.385(2)	O(13)-H(13A)	0.82
C(5)-H(5A)	0.97	C(19)-H(19)	0.93	O(14)-H(14A)	0.82
C(5)-H(5B)	0.97	C(20)-C(21)	1.483(3)	O(15)-H(15A)	0.82
C(6)-O(3)	1.404(4)	C(21)-O(10)	1.258(2)	O(16)-H(16A)	0.82
C(6)-C(1)#1	1.490(5)	C(21)-O(11)	1.270(2)	O(17)-H(17A)	0.82
C(6)-H(6A)	0.97	C(22)-O(12)	1.248(2)	O(18)-H(18C)	0.82
C(6)-H(6B)	0.97	C(22)-O(13)	1.287(2)	O(19)-H(19A)	0.923(17)
C(7)-O(4)	1.359(2)	C(23)-C(28)	1.387(3)	O(19)-H(19B)	0.892(17)
C(7)-C(12)	1.391(3)	C(23)-C(24)	1.391(3)	O(20)-H(20A)	0.895(17)
C(7)-C(8)	1.392(3)	C(23)-C(29)	1.483(3)	O(20)-H(20B)	0.871(17)
C(8)-C(9)	1.385(3)	C(24)-C(25)	1.389(3)	O(21)-H(21A)	0.882(18)
C(8)-H(8)	0.93	C(24)-H(24)	0.93	O(21)-H(21B)	0.910(17)
C(9)-C(10)	1.388(3)	C(25)-O(18)	1.367(2)	O(22)-H(22A)	0.907(17)
C(9)-C(14)	1.488(3)	C(25)-C(26)	1.386(3)	O(22)-H(22B)	0.904(17)
C(10)-C(11)	1.392(3)	C(26)-C(27)	1.391(3)	O(23)-H(23A)	0.888(17)
C(10)-H(10)	0.93	C(26)-H(26)	0.93	O(23)-H(23B)	0.898(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+2

Table S1b Bond lengths [Å] for **II**

C(1)-O(1)	1.395(4)	C(7)-C(13)	1.482(2)
C(1)-C(2)	1.479(5)	C(8)-C(9)	1.389(2)
C(1)-H(1A)	0.97	C(8)-H(8)	0.93
C(1)-H(1B)	0.97	C(9)-C(10)	1.388(2)
C(2)-O(2)	1.427(4)	C(9)-C(14)	1.497(2)
C(2)-H(2A)	0.97	C(10)-C(11)	1.395(3)
C(2)-H(2B)	0.97	C(10)-H(10)	0.93
C(3)-O(2)	1.412(4)	C(11)-C(12)	1.386(3)
C(3)-C(4)	1.457(6)	C(11)-C(15)	1.490(2)
C(3)-H(3A)	0.97	C(12)-H(12)	0.93
C(3)-H(3B)	0.97	C(13)-O(5)	1.234(2)
C(4)-O(3)	1.434(4)	C(13)-O(4)	1.289(2)
C(4)-H(4A)	0.97	C(14)-O(7)	1.216(2)
C(4)-H(4B)	0.97	C(14)-O(6)	1.303(2)
C(5)-O(3)	1.396(4)	C(15)-O(9)	1.194(2)
C(5)-C(6)	1.471(5)	C(15)-O(8)	1.312(2)
C(5)-H(5A)	0.97	O(1)-C(6)#1	1.436(4)
C(5)-H(5B)	0.97	O(4)-H(4)	0.82
C(6)-O(1)#1	1.436(4)	O(6)-H(6)	0.82
C(6)-H(6A)	0.97	O(8)-H(8A)	0.82
C(6)-H(6B)	0.97	O(10)-H(10B)	0.833(17)
C(7)-C(8)	1.392(3)	O(10)-H(10A)	0.848(17)
C(7)-C(12)	1.392(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2

Table S2a Bond angles [°] for **I**

O(1)-C(1)-C(6)#1	111.0(2)	C(16)-C(17)-C(18)	119.70(17)
O(1)-C(1)-H(1A)	109.4	C(16)-C(17)-H(17)	120.2
C(6)#1-C(1)-H(1A)	109.4	C(18)-C(17)-H(17)	120.2
O(1)-C(1)-H(1B)	109.4	C(19)-C(18)-C(17)	120.92(16)
C(6)#1-C(1)-H(1B)	109.4	C(19)-C(18)-C(22)	118.43(17)
H(1A)-C(1)-H(1B)	108	C(17)-C(18)-C(22)	120.64(17)
O(1)-C(2)-C(3)	108.7(2)	C(20)-C(19)-C(18)	118.81(17)
O(1)-C(2)-H(2A)	110	C(20)-C(19)-H(19)	120.6
C(3)-C(2)-H(2A)	110	C(18)-C(19)-H(19)	120.6
O(1)-C(2)-H(2B)	110	C(19)-C(20)-C(15)	120.50(17)
C(3)-C(2)-H(2B)	110	C(19)-C(20)-C(21)	119.86(17)
H(2A)-C(2)-H(2B)	108.3	C(15)-C(20)-C(21)	119.64(16)
O(2)-C(3)-C(2)	109.9(2)	O(10)-C(21)-O(11)	123.55(17)
O(2)-C(3)-H(3A)	109.7	O(10)-C(21)-C(20)	118.62(17)
C(2)-C(3)-H(3A)	109.7	O(11)-C(21)-C(20)	117.82(16)
O(2)-C(3)-H(3B)	109.7	O(12)-C(22)-O(13)	123.85(17)
C(2)-C(3)-H(3B)	109.7	O(12)-C(22)-C(18)	119.58(17)
H(3A)-C(3)-H(3B)	108.2	O(13)-C(22)-C(18)	116.56(17)
O(2)-C(4)-C(5)	108.7(2)	C(28)-C(23)-C(24)	120.84(17)
O(2)-C(4)-H(4A)	109.9	C(28)-C(23)-C(29)	120.63(17)
C(5)-C(4)-H(4A)	109.9	C(24)-C(23)-C(29)	118.53(17)
O(2)-C(4)-H(4B)	109.9	C(25)-C(24)-C(23)	119.85(17)
C(5)-C(4)-H(4B)	109.9	C(25)-C(24)-H(24)	120.1
H(4A)-C(4)-H(4B)	108.3	C(23)-C(24)-H(24)	120.1
O(3)-C(5)-C(4)	110.4(2)	O(18)-C(25)-C(26)	117.80(16)
O(3)-C(5)-H(5A)	109.6	O(18)-C(25)-C(24)	122.52(17)
C(4)-C(5)-H(5A)	109.6	C(26)-C(25)-C(24)	119.68(18)
O(3)-C(5)-H(5B)	109.6	C(25)-C(26)-C(27)	120.06(16)
C(4)-C(5)-H(5B)	109.6	C(25)-C(26)-H(26)	120
H(5A)-C(5)-H(5B)	108.1	C(27)-C(26)-H(26)	120
O(3)-C(6)-C(1)#1	111.3(3)	C(28)-C(27)-C(26)	120.67(17)
O(3)-C(6)-H(6A)	109.4	C(28)-C(27)-C(30)	119.27(17)
C(1)#1-C(6)-H(6A)	109.4	C(26)-C(27)-C(30)	120.06(16)
O(3)-C(6)-H(6B)	109.4	C(23)-C(28)-C(27)	118.85(18)
C(1)#1-C(6)-H(6B)	109.4	C(23)-C(28)-H(28)	120.6
H(6A)-C(6)-H(6B)	108	C(27)-C(28)-H(28)	120.6
O(4)-C(7)-C(12)	116.91(17)	O(14)-C(29)-O(15)	123.78(17)

O(4)-C(7)-C(8)	122.96(18)	O(14)-C(29)-C(23)	119.67(17)
C(12)-C(7)-C(8)	120.12(18)	O(15)-C(29)-C(23)	116.55(17)
C(9)-C(8)-C(7)	119.91(18)	O(16)-C(30)-O(17)	123.70(18)
C(9)-C(8)-H(8)	120	O(16)-C(30)-C(27)	118.53(16)
C(7)-C(8)-H(8)	120	O(17)-C(30)-C(27)	117.76(17)
C(8)-C(9)-C(10)	120.30(17)	C(1)-O(1)-C(2)	112.1(2)
C(8)-C(9)-C(14)	120.16(17)	C(4)-O(2)-C(3)	114.0(2)
C(10)-C(9)-C(14)	119.52(17)	C(6)-O(3)-C(5)	112.9(2)
C(9)-C(10)-C(11)	119.49(17)	C(7)-O(4)-H(4C)	109.5
C(9)-C(10)-H(10)	120.3	C(14)-O(5)-H(5C)	109.5
C(11)-C(10)-H(10)	120.3	C(14)-O(6)-H(6C)	109.5
C(12)-C(11)-C(10)	120.59(17)	C(13)-O(7)-H(7A)	109.5
C(12)-C(11)-C(13)	119.97(17)	C(13)-O(8)-H(8A)	109.5
C(10)-C(11)-C(13)	119.45(17)	C(16)-O(9)-H(9C)	109.5
C(11)-C(12)-C(7)	119.57(17)	C(21)-O(10)-H(10A)	109.5
C(11)-C(12)-H(12)	120.2	C(21)-O(11)-H(11A)	109.5
C(7)-C(12)-H(12)	120.2	C(22)-O(12)-H(12A)	109.5
O(7)-C(13)-O(8)	123.37(17)	C(22)-O(13)-H(13A)	109.5
O(7)-C(13)-C(11)	118.45(17)	C(29)-O(14)-H(14A)	109.5
O(8)-C(13)-C(11)	118.18(17)	C(29)-O(15)-H(15A)	109.5
O(6)-C(14)-O(5)	123.70(18)	C(30)-O(16)-H(16A)	109.5
O(6)-C(14)-C(9)	117.73(17)	C(30)-O(17)-H(17A)	109.5
O(5)-C(14)-C(9)	118.56(17)	C(25)-O(18)-H(18C)	109.5
C(20)-C(15)-C(16)	120.36(16)	H(19A)-O(19)-H(19B)	107(2)
C(20)-C(15)-H(15)	119.8	H(20A)-O(20)-H(20B)	113(2)
C(16)-C(15)-H(15)	119.8	H(21A)-O(21)-H(21B)	109(2)
O(9)-C(16)-C(17)	117.52(16)	H(22A)-O(22)-H(22B)	107(2)
O(9)-C(16)-C(15)	122.78(16)	H(23A)-O(23)-H(23B)	111(2)
C(17)-C(16)-C(15)	119.70(17)	C(23)-C(28)-C(27)	118.85(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+2

Table S2b Bond angles [°] for **II**

O(1)-C(1)-C(2)	108.7(2)	H(6A)-C(6)-H(6B)	108.2
O(1)-C(1)-H(1A)	110	C(8)-C(7)-C(12)	120.02(16)
C(2)-C(1)-H(1A)	110	C(8)-C(7)-C(13)	119.20(16)
O(1)-C(1)-H(1B)	110	C(12)-C(7)-C(13)	120.78(16)
C(2)-C(1)-H(1B)	110	C(9)-C(8)-C(7)	120.33(16)
H(1A)-C(1)-H(1B)	108.3	C(9)-C(8)-H(8)	119.8
O(2)-C(2)-C(1)	110.9(3)	C(7)-C(8)-H(8)	119.8
O(2)-C(2)-H(2A)	109.5	C(10)-C(9)-C(8)	119.38(16)
C(1)-C(2)-H(2A)	109.5	C(10)-C(9)-C(14)	119.08(15)
O(2)-C(2)-H(2B)	109.5	C(8)-C(9)-C(14)	121.53(15)
C(1)-C(2)-H(2B)	109.5	C(9)-C(10)-C(11)	120.53(16)
H(2A)-C(2)-H(2B)	108	C(9)-C(10)-H(10)	119.7
O(2)-C(3)-C(4)	109.6(3)	C(11)-C(10)-H(10)	119.7
O(2)-C(3)-H(3A)	109.8	C(12)-C(11)-C(10)	119.85(16)
C(4)-C(3)-H(3A)	109.8	C(12)-C(11)-C(15)	119.23(16)
O(2)-C(3)-H(3B)	109.8	C(10)-C(11)-C(15)	120.91(16)
C(4)-C(3)-H(3B)	109.8	C(11)-C(12)-C(7)	119.88(16)
H(3A)-C(3)-H(3B)	108.2	C(11)-C(12)-H(12)	120.1
O(3)-C(4)-C(3)	109.3(3)	C(7)-C(12)-H(12)	120.1
O(3)-C(4)-H(4A)	109.8	O(5)-C(13)-O(4)	123.58(17)
C(3)-C(4)-H(4A)	109.8	O(5)-C(13)-C(7)	120.62(17)
O(3)-C(4)-H(4B)	109.8	O(4)-C(13)-C(7)	115.79(16)
C(3)-C(4)-H(4B)	109.8	O(7)-C(14)-O(6)	123.47(17)
H(4A)-C(4)-H(4B)	108.3	O(7)-C(14)-C(9)	122.94(16)
O(3)-C(5)-C(6)	108.3(2)	O(6)-C(14)-C(9)	113.58(15)
O(3)-C(5)-H(5A)	110	O(9)-C(15)-O(8)	123.47(18)
C(6)-C(5)-H(5A)	110	O(9)-C(15)-C(11)	124.48(18)
O(3)-C(5)-H(5B)	110	O(8)-C(15)-C(11)	112.05(16)
C(6)-C(5)-H(5B)	110	C(1)-O(1)-C(6)#1	112.1(3)
H(5A)-C(5)-H(5B)	108.4	C(3)-O(2)-C(2)	112.0(3)
O(1)#1-C(6)-C(5)	109.8(2)	C(5)-O(3)-C(4)	113.2(3)
O(1)#1-C(6)-H(6A)	109.7	C(13)-O(4)-H(4)	109.5
C(5)-C(6)-H(6A)	109.7	C(14)-O(6)-H(6)	109.5
O(1)#1-C(6)-H(6B)	109.7	C(15)-O(8)-H(8A)	109.5
C(5)-C(6)-H(6B)	109.7	H(10B)-O(10)-H(10A)	112(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2

Table S3a Torsion angles [°] for **I**

O(1)-C(2)-C(3)-O(2)	66.0(3)	C(19)-C(20)-C(21)-O(10)	174.73(19)
O(2)-C(4)-C(5)-O(3)	-66.0(3)	C(15)-C(20)-C(21)-O(10)	-4.3(3)
O(4)-C(7)-C(8)-C(9)	-180.0(2)	C(19)-C(20)-C(21)-O(11)	-4.3(3)
C(12)-C(7)-C(8)-C(9)	1.5(3)	C(15)-C(20)-C(21)-O(11)	176.67(19)
C(7)-C(8)-C(9)-C(10)	0.2(3)	C(19)-C(18)-C(22)-O(12)	-1.2(3)
C(7)-C(8)-C(9)-C(14)	-178.62(19)	C(17)-C(18)-C(22)-O(12)	178.57(18)
C(8)-C(9)-C(10)-C(11)	-1.5(3)	C(19)-C(18)-C(22)-O(13)	179.39(18)
C(14)-C(9)-C(10)-C(11)	177.30(18)	C(17)-C(18)-C(22)-O(13)	-0.8(3)
C(9)-C(10)-C(11)-C(12)	1.2(3)	C(28)-C(23)-C(24)-C(25)	-1.4(3)
C(9)-C(10)-C(11)-C(13)	-178.42(17)	C(29)-C(23)-C(24)-C(25)	178.37(18)
C(10)-C(11)-C(12)-C(7)	0.4(3)	C(23)-C(24)-C(25)-O(18)	-178.37(19)
C(13)-C(11)-C(12)-C(7)	-179.94(19)	C(23)-C(24)-C(25)-C(26)	2.4(3)
O(4)-C(7)-C(12)-C(11)	179.56(19)	O(18)-C(25)-C(26)-C(27)	179.46(18)
C(8)-C(7)-C(12)-C(11)	-1.8(3)	C(24)-C(25)-C(26)-C(27)	-1.3(3)
C(12)-C(11)-C(13)-O(7)	-179.95(18)	C(25)-C(26)-C(27)-C(28)	-0.8(3)
C(10)-C(11)-C(13)-O(7)	-0.3(3)	C(25)-C(26)-C(27)-C(30)	178.70(18)
C(12)-C(11)-C(13)-O(8)	-0.7(3)	C(24)-C(23)-C(28)-C(27)	-0.7(3)
C(10)-C(11)-C(13)-O(8)	178.91(18)	C(29)-C(23)-C(28)-C(27)	179.52(18)
C(8)-C(9)-C(14)-O(6)	-174.29(19)	C(26)-C(27)-C(28)-C(23)	1.8(3)
C(10)-C(9)-C(14)-O(6)	6.9(3)	C(30)-C(27)-C(28)-C(23)	-177.73(17)
C(8)-C(9)-C(14)-O(5)	6.2(3)	C(28)-C(23)-C(29)-O(14)	-176.0(2)
C(10)-C(9)-C(14)-O(5)	-172.59(19)	C(24)-C(23)-C(29)-O(14)	4.2(3)
C(20)-C(15)-C(16)-O(9)	179.74(18)	C(28)-C(23)-C(29)-O(15)	3.2(3)
C(20)-C(15)-C(16)-C(17)	-1.2(3)	C(24)-C(23)-C(29)-O(15)	-176.59(19)
O(9)-C(16)-C(17)-C(18)	-179.62(17)	C(28)-C(27)-C(30)-O(16)	2.6(3)
C(15)-C(16)-C(17)-C(18)	1.3(3)	C(26)-C(27)-C(30)-O(16)	-176.99(18)
C(16)-C(17)-C(18)-C(19)	-0.1(3)	C(28)-C(27)-C(30)-O(17)	-178.68(18)
C(16)-C(17)-C(18)-C(22)	-179.92(18)	C(26)-C(27)-C(30)-O(17)	1.8(3)
C(17)-C(18)-C(19)-C(20)	-1.1(3)	C(6)#1-C(1)-O(1)-C(2)	-175.3(2)
C(22)-C(18)-C(19)-C(20)	178.70(17)	C(3)-C(2)-O(1)-C(1)	-179.9(2)
C(18)-C(19)-C(20)-C(15)	1.1(3)	C(5)-C(4)-O(2)-C(3)	172.4(2)
C(18)-C(19)-C(20)-C(21)	-177.92(18)	C(2)-C(3)-O(2)-C(4)	-169.0(2)
C(16)-C(15)-C(20)-C(19)	0.0(3)	C(1)#1-C(6)-O(3)-C(5)	170.2(2)
C(16)-C(15)-C(20)-C(21)	179.07(18)	C(4)-C(5)-O(3)-C(6)	176.6(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+2

Table S3b Torsion angles [°] for **II**

O(1)-C(1)-C(2)-O(2)	74.3(3)	C(12)-C(7)-C(13)-O(5)	175.19(18)
O(2)-C(3)-C(4)-O(3)	-70.1(4)	C(8)-C(7)-C(13)-O(4)	176.72(18)
O(3)-C(5)-C(6)-O(1)#1	66.0(3)	C(12)-C(7)-C(13)-O(4)	-3.5(3)
C(12)-C(7)-C(8)-C(9)	0.2(3)	C(10)-C(9)-C(14)-O(7)	-0.6(3)
C(13)-C(7)-C(8)-C(9)	179.96(17)	C(8)-C(9)-C(14)-O(7)	-179.74(18)
C(7)-C(8)-C(9)-C(10)	-0.4(3)	C(10)-C(9)-C(14)-O(6)	178.51(17)
C(7)-C(8)-C(9)-C(14)	178.74(16)	C(8)-C(9)-C(14)-O(6)	-0.6(3)
C(8)-C(9)-C(10)-C(11)	0.2(3)	C(12)-C(11)-C(15)-O(9)	-3.5(3)
C(14)-C(9)-C(10)-C(11)	-178.92(16)	C(10)-C(11)-C(15)-O(9)	176.8(2)
C(9)-C(10)-C(11)-C(12)	0.1(3)	C(12)-C(11)-C(15)-O(8)	176.67(19)
C(9)-C(10)-C(11)-C(15)	179.86(17)	C(10)-C(11)-C(15)-O(8)	-3.1(3)
C(10)-C(11)-C(12)-C(7)	-0.3(3)	C(2)-C(1)-O(1)-C(6)#1	175.1(2)
C(15)-C(11)-C(12)-C(7)	179.98(17)	C(4)-C(3)-O(2)-C(2)	178.9(3)
C(8)-C(7)-C(12)-C(11)	0.1(3)	C(1)-C(2)-O(2)-C(3)	-177.9(3)
C(13)-C(7)-C(12)-C(11)	-179.64(17)	C(6)-C(5)-O(3)-C(4)	-177.9(2)
C(8)-C(7)-C(13)-O(5)	-4.6(3)	C(3)-C(4)-O(3)-C(5)	173.8(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+2

Table S4 Crystal systems and space groups of some carboxylic acid derivatives complexed with 18-crown-6

Specimen	System	Space group	C/N*	Ref
18C6- 4-aminobenzoic acid	Monoclinic	$P2_1/n$	(C)	Boardman *et al*., 2014
18C6- 3,5-dinitrobenzoic acid	Triclinic	Pī	(C)	Boardman *et al*., 2014
cis,cis-1,3,5-cyclohexanetricarboxylic acid – 18C6	Rhombohedral	R-3*m*	(C)	Bhogala & Nangia, 2006
Hydroxylammonium Cyclohexane-3*cis*,5*cis*-dicarboxylic acid-1-carboxylate – 18C6	Monoclinic	$P2_1/c$	(C)	Bhogala & Nangia, 2006
Ammonium cyclohexane-3*cis*,5*cis*-dicarboxylic acid-1-carboxylate - 18C6 – Hydrate	Orthorhombic	$Pna2_1$	(N)	Bhogala & Nangia, 2006
18C6.5-nitroisophthalic acid.3(H_2O)	Orthorhombic	$Pca2_1$	(N)	Balakrishnan *et al.,* 2019
18C6.5-nitroisophthalic acid.CH_3OH. 2(H_2O)	Monoclinic	$P2_1/c$	(C)	Balakrishnan *et al.,* 2019
18C6- 5-Hydroxyisophthalic acid.10H_2O	Triclinic	Pī	(C)	Present Study
18C6- Trimesic acid.2H_2O	Triclinic	Pī	(C)	Present Study

*C- Centrosymmetry, N- Noncentrosymmetry

Table S5 Comparison of third-order nonlinear susceptibility ($\chi^{(3)}$) values

Specimen	**$\chi^{(3)}$ (esu)**	**Ref**
KDP	4×10^{-14}	Wang *et al*., 2016
[(15C5)4Pc]Ru(pyz)$_2$	1.94×10^{-10}	Gorbunova *et al*., 2015
[(15C5)$_4$Pc]Ga(OH)	1.85×10^{-10}	Vannikov *et al.,* 2011
[(15C5)$_4$Pc]In(OH)	1.34×10^{-9}	Grishina *et al.,* 2014
I	1.81×10^{-7}	**Present work**
II	3.34×10^{-7}	**Present work**

Table S6a Mulliken atomic charges of **I**

Atoms	Charge (e)	Atoms	Charge (e)	Atoms	Charge (e)	Atoms	Charge (e)
C1	-0.2830	H48	0.3882	H95	0.3913	H142	0.3856
H2	0.2232	C49	0.2721	C96	0.1272	O143	-0.3985
H3	0.2392	C50	-0.5146	C97	0.1328	C144	0.2854
C4	-0.3064	H51	0.3933	O98	-0.2748	C145	-0.5470
H5	0.2346	C52	0.1322	H99	0.3852	H146	0.3528
H6	0.2525	C53	0.1317	O100	-0.4078	C147	0.2661
C7	-0.3026	O54	-0.3771	O101	-0.3011	C148	-0.5106
H8	0.2565	H55	0.3248	H102	0.3869	H149	0.3918
H9	0.2345	O56	-0.3030	O103	-0.3807	C150	0.2686
C10	-0.3076	H57	0.3870	O104	-0.3813	C151	-0.5050
H11	0.2387	O58	-0.3819	H105	0.3252	H152	0.3926
H12	0.2441	O59	-0.2945	C106	0.2574	C153	0.1272
C13	-0.3095	H60	0.3882	C107	-0.5446	C154	0.1340
H14	0.2576	O61	-0.3878	H108	0.3522	O155	-0.2763
H15	0.2444	C62	-0.5431	C109	0.2968	H156	0.3849
C16	-0.2811	H63	0.3783	C110	-0.5122	O157	-0.4046
H17	0.2188	C64	0.2461	H111	0.3877	O158	-0.2988
H18	0.2488	C65	-0.5142	C112	0.2731	H159	0.3871
O19	-0.3645	H66	0.3946	C113	-0.5156	O16	-0.3830
O20	-0.3742	C67	0.2663	H114	0.3926	O161	-0.3833
O21	-0.3701	C68	-0.5110	C115	0.1330	H162	0.3245
C22	-0.2906	H69	0.3885	C116	0.1315	O163	-0.7839
H23	0.2544	C70	0.2750	O117	-0.3770	H164	0.4124
H24	0.2345	C71	0.1335	H118	0.3253	H165	0.3995
C25	-0.2992	C72	0.1276	O119	-0.3018	O166	-0.7482
H26	0.2388	O73	-0.3296	H120	0.3868	H167	0.3868
H27	0.2494	H74	0.1602	O121	-0.3842	H168	0.3130
C28	-0.3085	O75	-0.2847	O122	-0.2946	O169	-0.8090
H29	0.2580	H76	0.3860	H123	0.3872	H170	0.4217
H30	0.2385	O77	-0.3932	O124	-0.3898	H171	0.4014
C31	-0.3047	O78	-0.2829	C125	-0.5456	O172	-0.7503
H32	0.2404	H79	0.3857	H126	0.3674	H173	0.3203
H33	0.2443	O80	-0.3973	C127	0.2533	H174	0.3920
C34	-0.3082	O81	-0.7603	C128	-0.5206	O175	-0.7470
H35	0.2499	H82	0.3946	H129	0.3945	H176	0.3830
H36	0.2460	H83	0.3798	C130	0.2625	H177	0.3218
C37	-0.2805	O84	-0.7865	C131	-0.5208	O178	-0.6301
H38	0.2184	H85	0.4137	H132	0.3843	O179	-0.6708
H39	0.2486	H86	0.4069	C133	0.2823	O180	-0.7369
O40	-0.3697	C87	0.2855	C134	0.1260	H181	0.3831
O41	-0.3807	C88	-0.5451	C135	0.1246	H182	0.3921
O42	-0.3676	H89	0.3534	O136	-0.3992	H183	0.3690
C43	0.2570	C90	0.2662	H137	0.3703	H184	0.3796
C44	-0.5453	C91	-0.5087	O138	-0.2950	H185	0.3388
H45	0.3518	H92	0.3927	H139	0.3855	H186	0.3239
C46	0.2968	C93	0.2689	O140	-0.3982		
C47	-0.5104	C94	-0.5097	O141	-0.2847		

Table S6b Mulliken atomic charges of **II**

Atoms	Charge (e)	Atoms	Charge (e)	Atoms	Charge (e)	Atoms	Charge (e)
C1	-0.0129	H24	0.1483	C47	0.0683	C70	-0.2491
H2	0.0897	C25	-0.0056	H48	0.1265	C71	0.0659
H3	0.1483	H26	0.0983	C49	-0.2502	H72	0.1324
C4	-0.0056	H27	0.1147	C50	0.0700	C73	-0.2528
H5	0.0983	C28	0.0029	H51	0.1290	C74	0.0683
H6	0.1147	H29	0.1298	C52	0.4337	H75	0.1265
C7	0.0029	H30	0.0915	C53	0.4701	C76	-0.2502
H8	0.1298	C31	-0.0218	C54	0.4344	C77	0.0700
H9	0.0915	H32	0.1099	O55	-0.3315	H78	0.1290
C10	-0.0218	H33	0.0953	H56	0.2563	C79	0.4337
H11	0.1099	C34	-0.0330	O57	-0.3306	C80	0.4701
H12	0.0953	H35	0.0949	O58	-0.3702	C81	0.4344
C13	-0.0330	H36	0.1126	H59	0.3265	O82	-0.3315
H14	0.0949	C37	0.0044	O60	-0.3755	H83	0.2563
H15	0.1126	H38	0.0908	O61	-0.3321	O84	-0.3306
C16	0.0044	H39	0.1363	H62	0.2559	O85	-0.3702
H17	0.0908	O40	-0.4270	O63	-0.3297	H86	0.3265
H18	0.1363	O41	-0.4201	O64	-0.5581	O87	-0.3755
O19	-0.4270	O42	-0.3822	H65	0.2973	O88	-0.3321
O20	-0.4201	C43	-0.2491	H66	0.2966	H89	0.2559
O21	-0.3822	C44	0.0660	O67	-0.5581	O90	-0.3297
C22	-0.0129	H45	0.1325	H68	0.2974		
H23	0.0897	C46	-0.2528	H69	0.2966		