Synthesis, Crystal Growth, Physio-chemical Characterization and Quantum Chemical Calculations of NLO Active Metal-Organic Crystal: Dibromo (4-Hydroxy-L-Proline) Cadmium (II) for Nonlinear Optical Applications

K. Boopathi*[a], S. Moorthy Babu[a], R. Jagan[c], S. Athimoolam[d], P. Ramasamy[b]

[a]Crystal Growth Centre, Anna University, Chennai- 600 025
[b]SSN Research Centre, SSN College of Engineering, Kalavakkam-603110
[c]Department of Physics, St. Joseph College of Engineering, Chennai- 600119
[d]Department of Physics, University College of Engineering, Nagercoil, Anna University, Nagercoil-629 004

ELECTRONIC SUPPLEMENTARY INFORMATION

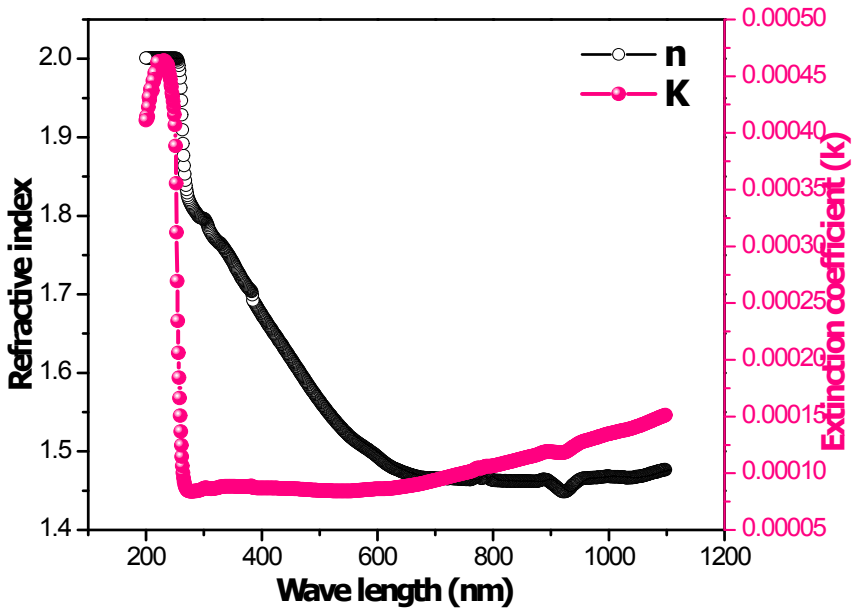

Figure. 11 (S1). (c) Plot of refractive index and extinction coefficient vs wavelength of DB4HPC Crystal

Table S1 details of Hydrogen bonds for DB4HPC

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...Br(1)#3	0.98	3	3.631(3)	123.1
C(3)-H(3A)...Br(1)#3	0.97	3.11	3.784(5)	128.3
C(3)-H(3B)...Br(2)	0.97	2.97	3.870(5)	154.5
C(5)-H(5A)...Br(1)#1	0.97	2.87	3.731(6)	148.8
N(1)-H(1A)...O(3)#4	0.89	2.09	2.825(6)	138.7
N(1)-H(1A)...Br(1)#3	0.89	3.09	3.757(5)	133.1
O(3)-H(3)...O(1)#5	0.82	2.41	3.016(5)	131.1
O(3)-H(3)...Br(2)#6	0.82	2.97	3.575(3)	133
C(2)-H(2)...Br(1)#3	0.98	3	3.631(3)	123.1
C(3)-H(3A)...Br(1)#3	0.97	3.11	3.784(5)	128.3
C(3)-H(3B)...Br(2)	0.97	2.97	3.870(5)	154.5
C(4)-H(4)...Br(2)#6	0.98	2.98	3.484(5)	112.9
C(5)-H(5A)...Br(1)#1	0.97	2.87	3.731(6)	148.8
N(1)-H(1A)...O(3)#4	0.89	2.09	2.825(6)	138.7
N(1)-H(1A)...Br(1)#3	0.89	3.09	3.757(5)	133.1
O(3)-H(3)...O(1)#5	0.82	2.41	3.016(5)	131.1
O(3)-H(3)...Br(2)#6	0.82	2.97	3.575(3)	133

Table S2 Bond Length for DB4HPC

Bond Length [Å]	
C(1)-O(2)	1.244(8)
C(1)-O(1)	1.261(7)
C(1)-C(2)	1.533(5)
C(2)-N(1)	1.495(7)
C(2)-C(3)	1.518(7)
C(2)-H(2)	0.98
C(3)-C(4)	1.540(6)
C(3)-H(3A)	0.97
C(3)-H(3B)	0.97
C(4)-O(3)	1.423(6)
C(4)-C(5)	1.513(6)
C(4)-H(4)	0.98

C(5)-N(1)	1.486(7)
C(5)-H(5A)	0.97
C(5)-H(5B)	0.97
N(1)-H(1A)	0.89
N(1)-H(1B)	0.89
O(1)-Cd(1)	2.369(3)
O(2)-Cd(1)#1	2.313(3)
O(3)-H(3)	0.82
Br(1)-Cd(1)#2	2.7378(6)
Br(1)-Cd(1)	2.7669(6)
Br(2)-Cd(1)	**2.7079(7)**
Br(2)-Cd(1)#2	2.7535(7)

Table S3 Bond angle for DB4HPC

Bond Angle [deg]	
O(2)-C(1)-O(1)	126.8(3)
O(2)-C(1)-C(2)	116.7(6)
O(1)-C(1)-C(2)	116.5(6)
N(1)-C(2)-C(3)	103.3(3)
N(1)-C(2)-C(1)	107.2(5)
C(3)-C(2)-C(1)	116.2(4)
N(1)-C(2)-H(2)	109.9
C(3)-C(2)-H(2)	109.9
C(1)-C(2)-H(2)	109.9
C(2)-C(3)-C(4)	106.2(4)
C(2)-C(3)-H(3A)	110.5
C(4)-C(3)-H(3A)	110.5
C(2)-C(3)-H(3B)	110.5
C(4)-C(3)-H(3B)	110.5
H(3A)-C(3)-H(3B)	108.7
O(3)-C(4)-C(5)	111.8(4)
O(3)-C(4)-C(3)	108.3(4)
C(5)-C(4)-C(3)	105.8(5)
O(3)-C(4)-H(4)	110.3
C(5)-C(4)-H(4)	110.3
C(3)-C(4)-H(4)	110.3
N(1)-C(5)-C(4)	105.0(4)
N(1)-C(5)-H(5A)	110.8
C(4)-C(5)-H(5A)	110.8
N(1)-C(5)-H(5B)	110.8
C(4)-C(5)-H(5B)	110.8
H(5A)-C(5)-H(5B)	108.8
C(5)-N(1)-C(2)	105.8(3)
C(5)-N(1)-H(1A)	110.6

C(2)-N(1)-H(1A)	110.6
C(5)-N(1)-H(1B)	110.6
C(2)-N(1)-H(1B)	110.6
H(1A)-N(1)-H(1B)	108.7
C(1)-O(1)-Cd(1)	121.5(2)
C(1)-O(2)-Cd(1)#1	130.3(3)
C(4)-O(3)-H(3)	109.5
Cd(1)#2-Br(1)-Cd(1)	85.662(10)
Cd(1)-Br(2)-Cd(1)#2	86.505(11)
O(2)#2-Cd(1)-O(1)	171.88(14)
O(2)#2-Cd(1)-Br(2)	96.04(10)
O(1)-Cd(1)-Br(2)	90.01(9)
O(2)#2-Cd(1)-Br(1)#1	92.93(9)
O(1)-Cd(1)-Br(1)#1	92.04(9)
Br(2)-Cd(1)-Br(1)#1	94.019(19)
O(2)#2-Cd(1)-Br(2)#1	83.03(10)
O(1)-Cd(1)-Br(2)#1	90.91(10)
Br(2)-Cd(1)-Br(2)#1	179.06(2)
Br(1)#1-Cd(1)-Br(2)#1	86.094(19)
O(2)#2-Cd(1)-Br(1)	85.82(9)
O(1)-Cd(1)-Br(1)	89.16(9)
Br(2)-Cd(1)-Br(1)	86.410(19)
Br(1)#1-Cd(1)-Br(1)	178.716(15)
Br(2)#1-Cd(1)-Br(1)	93.458(19)

Table S4 The elements are present in the wt. % and at. %

Element	Wt%	At%
Cd	28.27	06.92
Br	32.39	11.15
N	03.96	7.78
O	12.17	20.94
C	23.21	53.20

Table S5. Comparative studies of metal-organic complexes

Compound name	Crystal System & space group	Transparency cut off	Thermal stability	SHG Efficiency [> KDP]	Reference
Dibromo bis (L-proline) zinc(II)	Orthorhombic $P2_12_12_1$	300 nm	Up to 229 ºC	1.5 times	[26]
Dibromo bis (L-proline) cadmium (II)	Orthorhombic $P2_12_12_1$	235 nm	Up to 218 ºC	2 times	[27]
Bis (L-proline) cadmium iodide	Orthorhombic $P2_12_12_1$	230 nm	Up to 180 ºC	2 times	[28]
Dichloro bis (L-proline) zinc (II)	Orthorhombic $P2_12_12_1$	240nm	Up to 243 ºC	0.5 times	[29]
Dichloro(4-hydroxy-l-proline) cadmium(II)	Monoclinic $P2_1$	200 nm	Up to 255 ºC	0.5 times	[30]
Dibromo (4-hydroxy L-proline) cadmium (II)	Monoclinic $P2_1$	251 nm	Up to 240 ºC	2.25 times	Present work

Table S6. Optimized molecular geometrical parameters for present compound

Atoms Connected	HF/ LANL2DZ	B3LYP/ LANL2DZ
Bond length (Å)		
C1–C2	1.534	1.545
C1–O15	1.293	1.273
C1–O16	1.218	1.310
C2–C4	1.518	1.554
C2–N12	1.510	1.541
C4–C7	1.545	1.542
C7–C9	1.507	1.535
C7–O17	1.421	1.472
C9–N12	1.482	1.527
Cd21-O15	2.368	2.484
Cd21–Br19	2.768	2.566
Cd21–Br20	2.707	2.656
Bond Angle (°)		
C2–C1–O15	114.4	120.7
C2–C1–O16	118.4	115.1
O15–C1–O16	127.2	123.9
C2–N12–C9	105.8	105.1
O15–Cd21–Br19	88.7	122.2
O15–Cd21–Br20	90.1	92.3
Br19–Cd21–Br20	86.4	141.4
Torsional Angle (°)		
C1–C2–C4–C7	-91.2	-116.4
N12–C2–C4–C7	24.4	-3.1
C1–C2–N12–C9	85.9	96.4
C4–C2–N12–C9	-37.5	-23.7
C2–C4–C7–C9	-3.3	28.5