Supplementary Information

Unprecedented 3D Coordination Polymeric Frameworks of 5-Aminoisophthalate with Alkaline Earth Metals (Sr and Ba): Synthesis, Analysis and Styrene Oxidation

Atom Rajiv Singh,[a] Anil Singh Rajpurohit,[b] Aribam Rishikanta Sharma, [a] Madhavan Jaccob[b], Raju Laishram[a] and Rajkumari Lonibala[a*]

[a]Department of Chemistry, Manipur University, Imphal,795003, Manipur, India. E-mail:lonirk@yahoo.co.uk

[b]Department of Chemistry & Loyola Institute of Frontier Energy (LIFE), Loyola College (Autonomous), Affiliated to University of Madras, Chennai-600034, India.

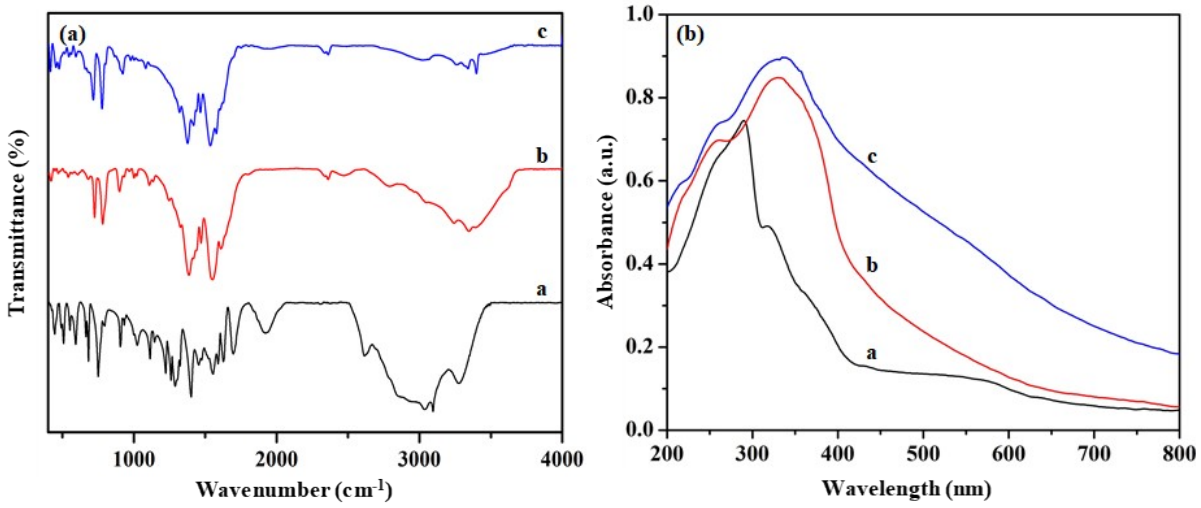


Figure S1 (a) FT-IR spectra and (b) DRS UV-Visible spectra of the (a) 5-AIP, (b & c) as-prepared 1 and 2 complexes, respectively.

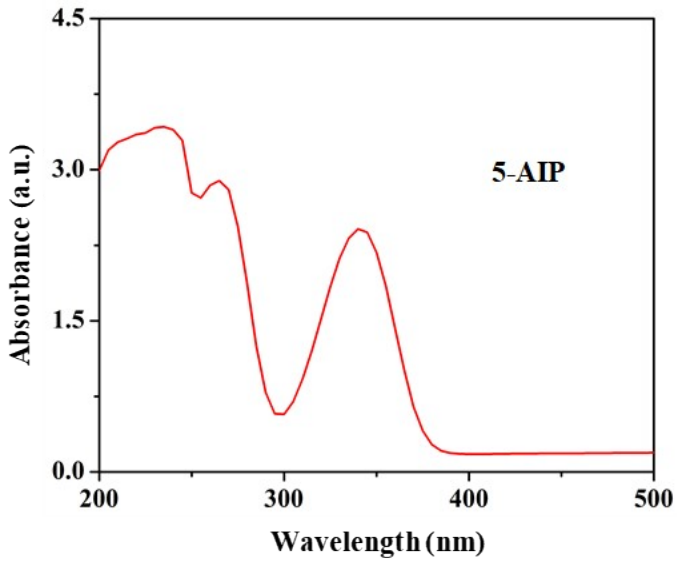


Figure S2 UV-Visible spectra of the 5-AIP dissolved in acetonitrile solvent.

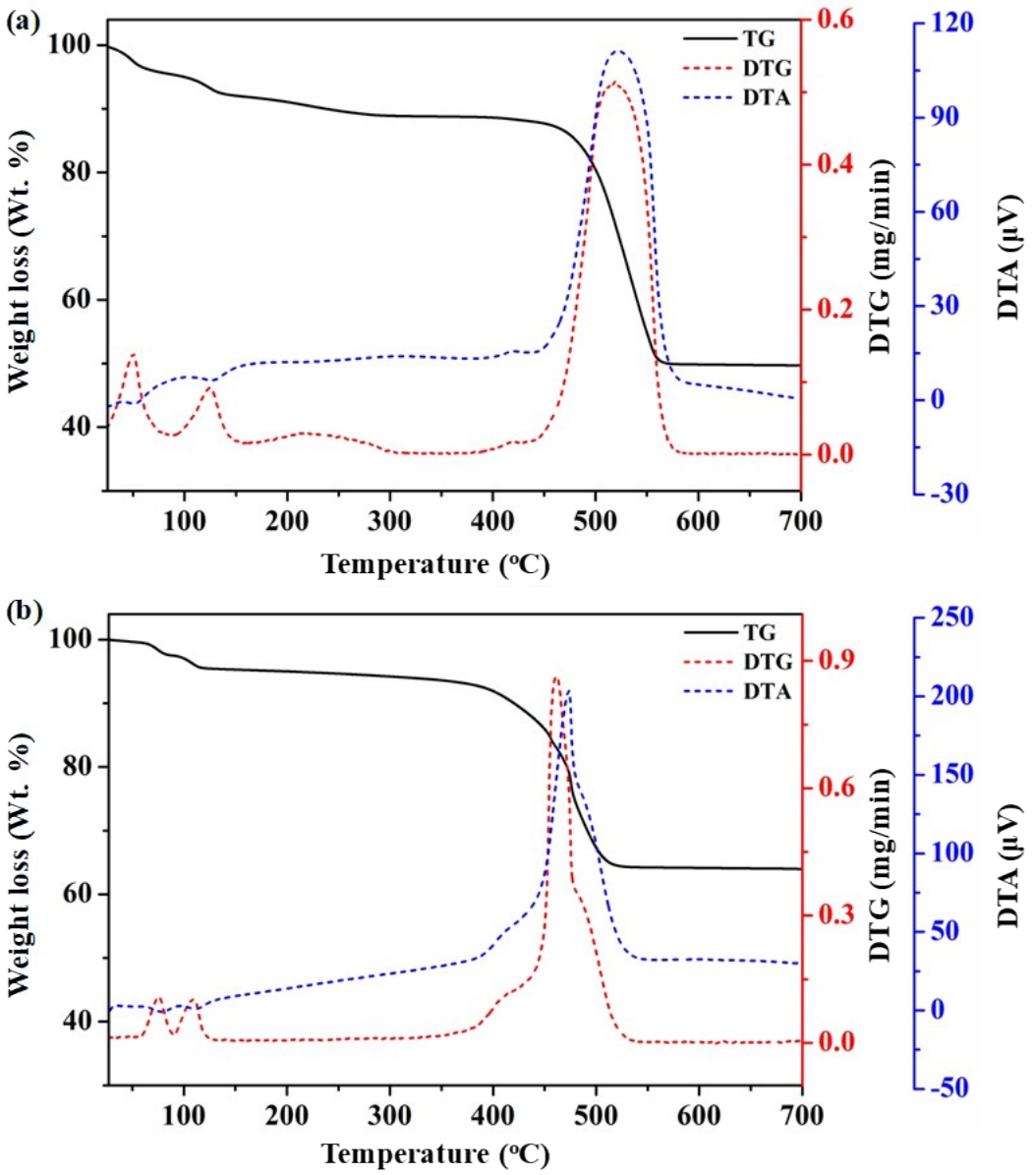


Figure S3 TGA, DTG and DTA curves of (a) 1 and (b) 2 complexes.

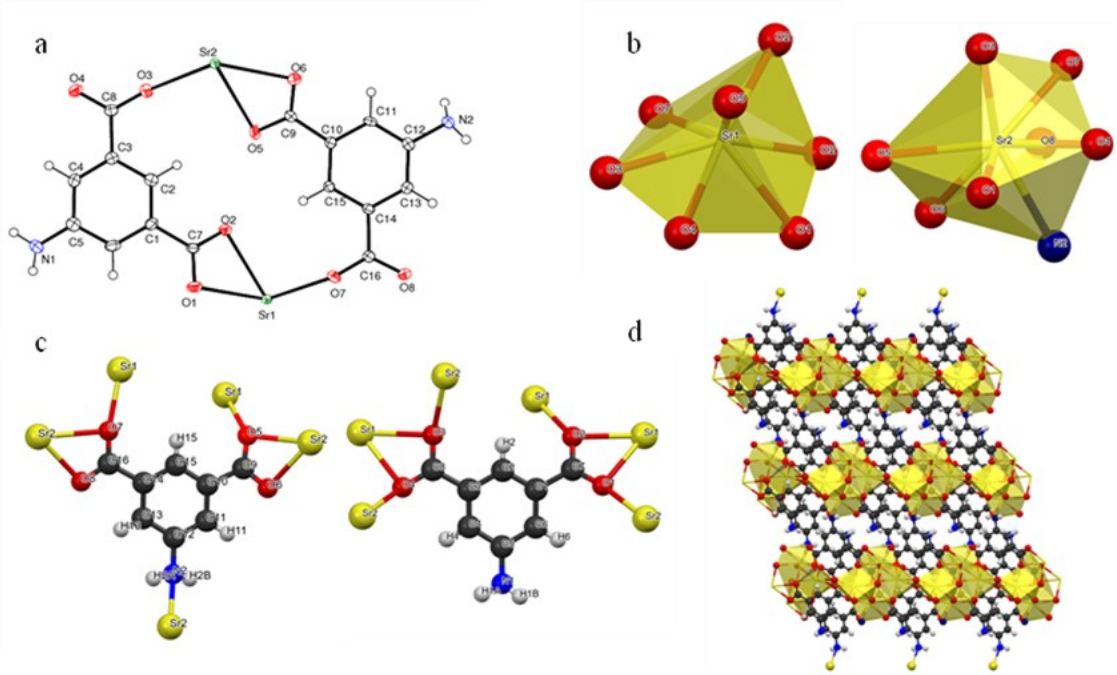


Figure S4 (a) ORTEP image of asymmetric unit of $[Sr_2(5\text{-AIP})_2]_n$,(b) Distorted capped trigonal prismatic (Sr1) and distorted bicapped trigonal prismatic(Sr2) of Sr with [Sr(1)-O(7), 2.424(3)Å], [Sr(1)-O(5)#1, 2.490(3)Å], [Sr(1)-O(2)#1, 2.540(3)Å], [Sr(1)-O(2), 2.642(3)Å], [Sr(1)-O(4)#2, 2.669(3)Å], [Sr(1)-O(1), 2.675(3)Å] and [Sr(1)-O(3)#2, 2.736(4)Å] for S1 and [Sr(2)-O(3), 2.510(4)Å], [Sr(2)-O(8)#4, 2.535(3) Å], [Sr(2)-O(6), 2.541(3) Å], [Sr(2)-O(1)#3, 2.552(3) Å], [Sr(2)-O(4)#5, 2.649(3) Å], [Sr(2)-N(2)#6, 2.756(4) Å], [Sr(2)-O(7)#4, 2.765(3) Å] and [Sr(2)-O(5), 2.780(3) Å]. Symmetry transformations used to generate equivalent atoms: (1) -x+2,-y+1,-z+1 (2) x+1,y-1,z (3) -x+1,-y+1,-z+1 (4) x-1,y+1,z (5) -x,-y+2,-z+1(6) -x+1,-y+1,-z+2, (c) (1) μ_2-η^2:η^1(O7,O8) tridentate, μ_2-η^1:η2(O5,O6) tridentate and μ1:η^1 (N2) monodentate and (2) μ_3-η1:η2:η1(O1,O2) tetradentate and μ_3-η1:η2:η1(O3,O4) tetradentate bridging binding modes of the 5-AIP along b-axis, (d) 3D structure of $[Sr_2(5\text{-AIP})_2]_n$ along a-axis.

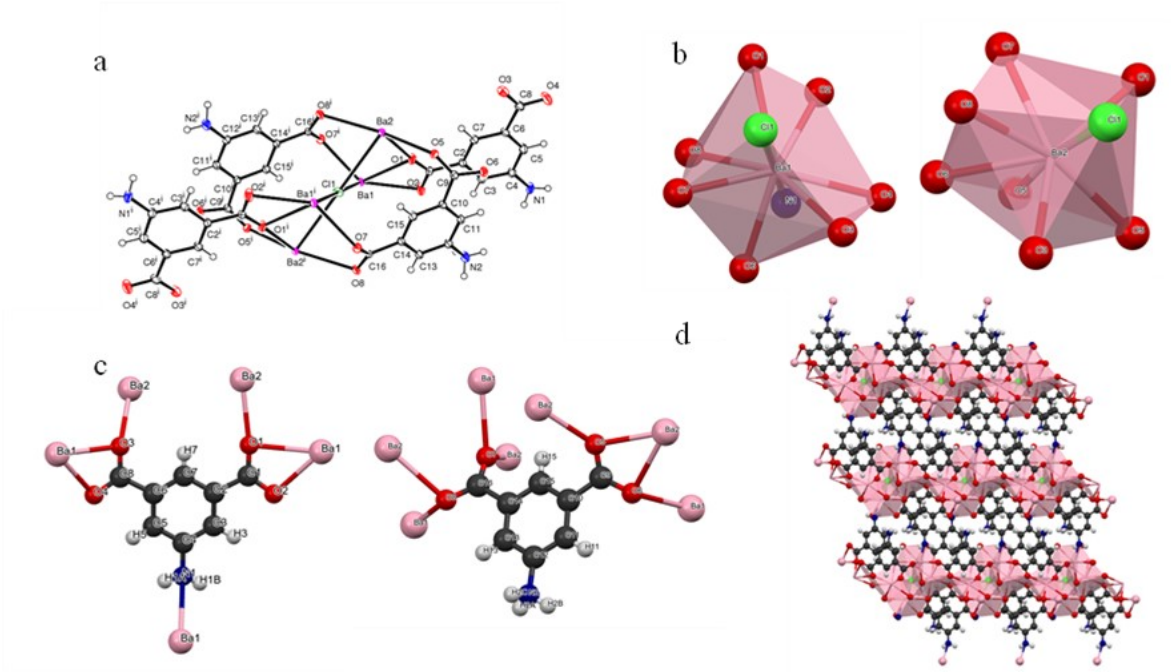


Figure S5 (a) ORTEP structure of asymmetric unit of Complex 2, (b) Ba1 (Distorted monocapped square antiprismatic) and Ba2 (Distorted square antiprismatic) of Ba in $[Ba_4(5AIP)_3(5HAIP)]_n$ with [Ba(1)-O(2) , 2.726(2)Å], [Ba(1)-O(6)#1, 2.747(2) Å], [Ba(1)-O(4)#2, 2.769(2) Å], [Ba(1)-O(7)#3, 2.785(2) Å], [Ba(1)-O(8)#4, 2.863(2) Å], [Ba(1)-O(3)#2, 2.865(2) Å], [Ba(1)-O(1), 2.943(2) Å], [Ba(1)-N(1)#5, 3.010(3) Å] and [Ba(1)-Cl(1), 3.14076(17) Å] for Ba1 and [Ba(2)-O(1), 2.642(2)Å], [Ba(2)-O(3)#7, 2.693(2) Å], [Ba(2)-O(5), 2.753(2) Å], [Ba(2)-O(7)#4, 2.765(2) Å], [Ba(2)-O(5)#7, 2.8371(19) Å], [Ba(2)-O(8)#3, 2.8547(19) Å], [Ba(2)-O(6)#7, 2.869(2) Å] and [Ba(2)-Cl(1), 3.25324(17) Å] for Ba2.Symmetry transformations used to generate equivalent atoms: (1) x,y+1,z (2) x-1,y+1,z (3) -x+1,-y+2,-z (4) x+1,y,z (5) -x+2,-y+2,-z-1 (7) -x+2,-y+1,-z (8) x+1,y-1,z, (c) (1) μ2-η2: η1(O4,O3) tridentate, μ3-η1:η2(O1,O2) tridentate and μ1-η1(N1) tetradentate modes and (2) μ4-η1:η1: η1: η1(O7,O8) tetradentate, μ4-η1:η2: η1(O5,O6) tetradentate of the 5-AIP in $[Ba_4(5AIP)_3(5HAIP)]_n$, (d) 3D structure of Complex **2** along **a**-axis.

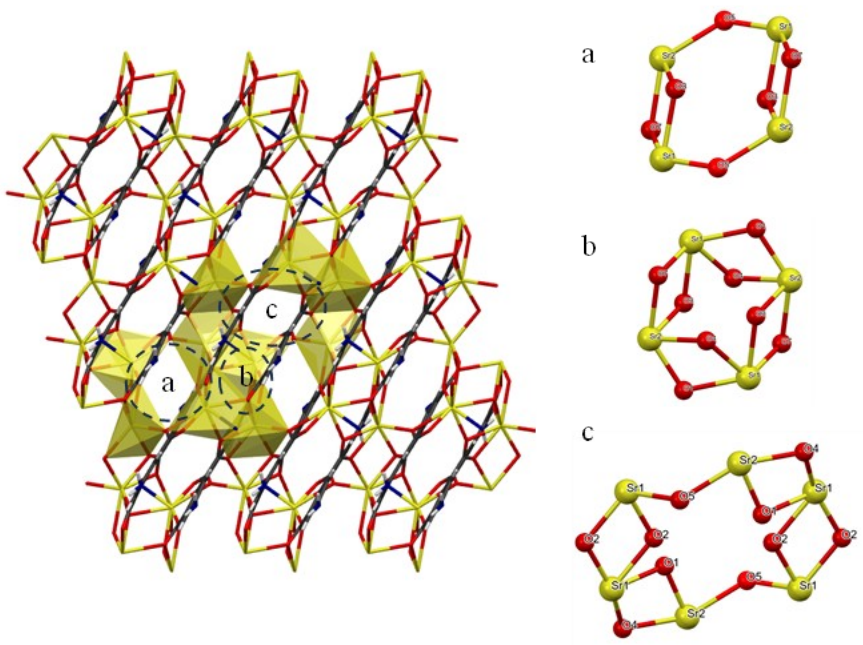


Figure S6 Perspective view of $[Sr_2(5\text{-}AIP)_2]_n$ along c-axis showing portion of Sr-O atoms forming two tetranuclear cluster $\{Sr_4O_6\}$, $\{Sr_4O_8\}$ and a hexanuclear cluster $\{Sr_6O_{10}\}$.

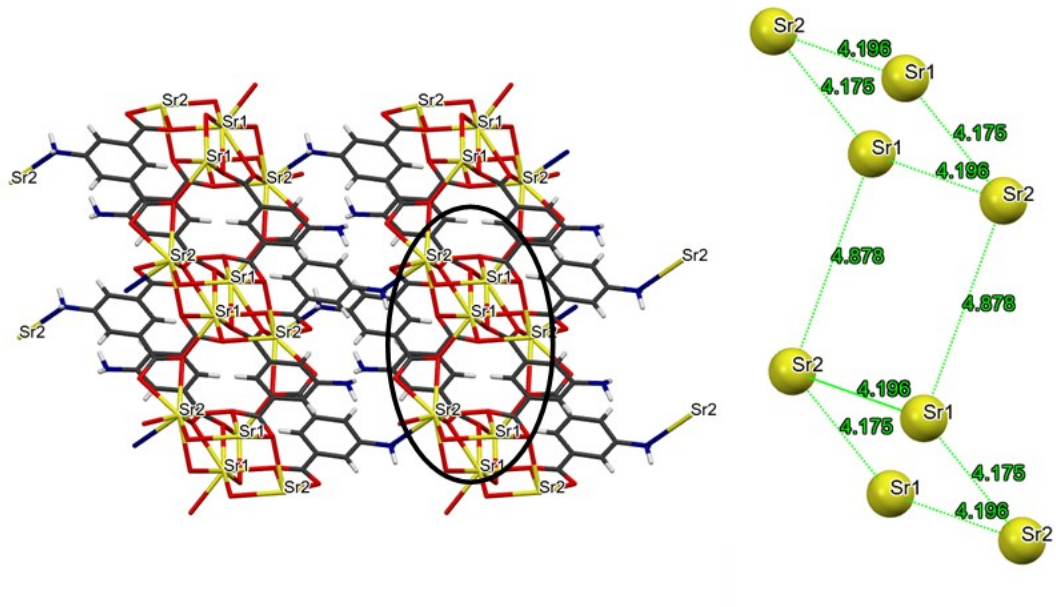


Figure S7 Perspective view of$[Sr_2(5AIP)_2]_n$ along b axis showing Ladder polymeric chain of Sr

Figure S8 Perspective view of 1D rod shape polymeric chain extending along a-axis showing infinite $(Sr\text{-}O)_n$ bond.

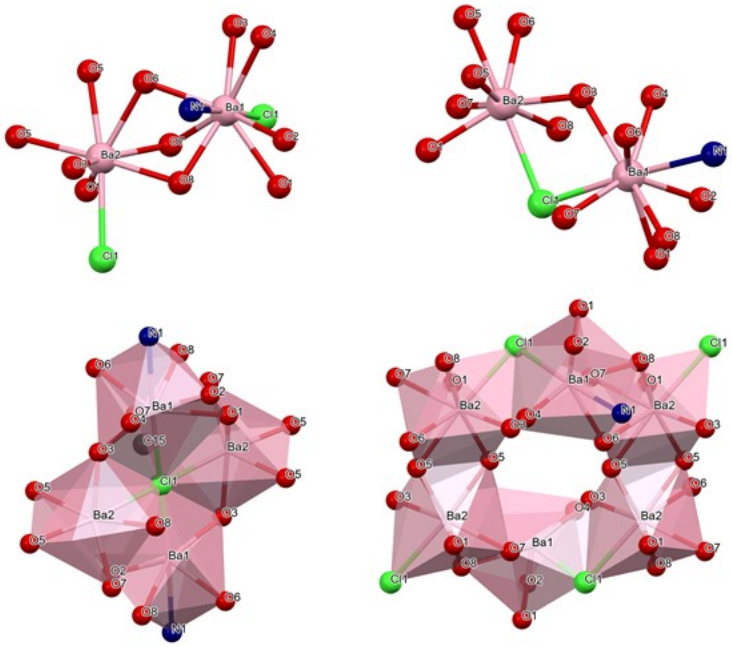


Figure S9 Dinuclear, Tetranuclear, hexanuclear array representation of 2

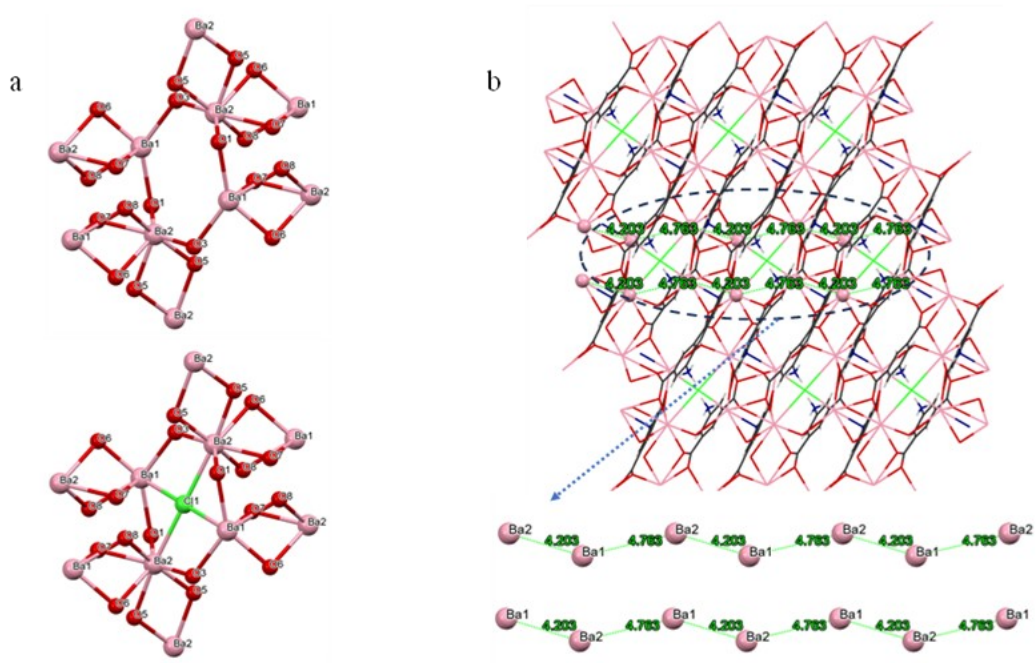


Figure S10 a){$Ba_{10}O_{20}$}unit showing only Ba-O bond (above) and{$Ba_{10}O_{20}Cl$} unit(below) and b) A portion of Ba-Cp showing Zig-zag ladder type coordination polymer(above) and showing Ba-Ba chain for clarity (below) along c –axis

Table S1 Crystallographic and structure refinement data for 1 and 2

Compounds	1	2
Empirical formula	$Sr_2C_{16}H_{10}N_2O_8$	$Ba_4C_{32}H_{21}ClN_4O_{16}$
Formula weight	533.50	1302.34
Temperature	293(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	*a* = 7.4671(2) Å *b* = 9.5062(3) Å *c* = 12.2972(4) Å	*a* = 7.210(2) Å *b* = 9.8113(2) Å *c* = 12.5148(3) Å
Volume	797.48(4) $Å^3$	860.27(4) $Å^3$
Z	2	1
Density (calculated)	2.222 mg/m^3	2.514 mg/m^3
Absorption coefficient	6.744 mm^{-1}	4.680 mm^{-1}
F(000)	520	610
Crystal size	0.150 x 0.100 x 0.100 mm^3	0.150 x 0.100 x 0.100 mm^3
Theta range for datacollection	2.324 to 27.998°.	2.458 to 29.997°.
Index ranges	$-9 \le h \le 9$, $-12 \le k \le 12$, $-15 \le l \le 16$	$-10 \le h \le 10$, $-13 \le k \le 13$, $-17 \le l \le 17$
Reflections collected	14336	32740
Independent reflections	3839 [$R_{(int)}$ = 0.0358]	5022 [$R_{(int)}$ = 0.0422]
Completeness to theta = 25.242°	99.9 %	99.9 %

Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.5365	0.7483 and 0.5251
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data/ restraints / parameters	3439 / 6 / 265	5022 / 9 / 279
Goodness-of-fit on F2	1.047	1.045
Final R indices [I>2sigma(I)]	$R_1 = 0.0448$, $wR_2 = 0.1267$	$R_1 = 0.0203$, $wR_2 = 0.0418$
R indices (all data)	$R_1 = 0.0609$, $wR_2 = 0.1377$	$R_1 = 0.0298$, $wR_2 = 0.0456$
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	2.207 and -0.552 e.Å^{-3}	0.801 and -0.709 e.Å^{-3}

Table S2 Hydrogen bonds for Complex **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1B)...O(6)#7	0.852(19)	2.26(4)	3.007(6)	146(5)
N(1)-H(1A)...O(8)#8	0.856(19)	2.37(4)	3.076(6)	140(5)
N(2)-H(2A)...O(4)#9	0.852(18)	2.43(5)	2.917(5)	117(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1 #2 x+1,y-1,z #3 -x+1,-y+1,-z+1
#4 x-1,y+1,z #5 -x,-y+2,-z+1 #6 -x+1,-y+1,-z+2
#7 x, y, z-1 #8 x-1,y+1,z-1 #9 x+1,y-1, z+1

Table S3 Hydrogen bonds for Complex **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(6)#11	0.839(17)	2.25(3)	2.864(3)	130(3)
N(1)-H(1B)...O(8)#12	0.841(17)	2.33(3)	2.981(3)	134(3)
N(2)-H(2A)...O(2)#12	0.859(17)	2.12(3)	2.828(4)	139(3)
N(2)-H(2B)...O(4)#11	0.850(17)	2.17(2)	2.939(4)	151(3)
N(2)-H(2C)...N(2)#12	0.862(18)	2.03(2)	2.885(7)	172(4)

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z #2 x-1,y+1,z #3 -x+1,-y+2,-z #4 x+1,y,z
#5 -x+2,-y+2,-z-1 #6 -x+2,-y+2,-z #7 -x+2,-y+1,-z
#8 x+1,y-1,z #9 x,y-1,z #10 x-1,y,z #11 -x+2,-y+1,-z-1
#12 -x+1,-y+2,-z-1

Table S4 Selected bond lengths (Å) and angles (deg.) for $[Sr_2(5AIP)_2]_n$(1)

Type of bond	Bond distance (Å)	Type of bond	Bond angle (deg.)
Sr1-O7	2.424	O7–Sr1–O5	132.65
Sr1-O5#1	2.490	O7–Sr1–O2#1	85.70
Sr1–O2#1	2.540	O5#1–Sr1–O2#1	81.25
Sr1–O2	2.642	O7–Sr1–O2	95.24
Sr1–O4#2	2.669	O2#1–Sr1–O2	68.02
Sr1–O1	2.675	O7–Sr1–O4#2	113.08
Sr1–O3#2	2.736	O5#1–Sr1–O4#2	77.97
Sr1–C7	3.027	O2#1–Sr1–O4#2	158.31
Sr1–C8#2	3.045	O2–Sr1-O4#2	118.31
Sr1–Sr2#3	4.1750	O5#1–Sr1–O1	108.74
Sr1–Sr2#2	4.1958	O2#1Sr1–O1	112.14
Sr1–Sr1#1	4.2962	O2–Sr1–O1	48.83
Sr2–O3	2.510	O4#2–Sr1–O1	69.53
Sr2–O8#4	2.535	Sr2#3–O1–Sr1	105.98
Sr2–O6	2.541	Sr1#1–O2–Sr1	111.98
Sr2–O1#3	2.552	Sr2–O3–Sr1#4	106.13
Sr2–O4#5	2.649	O3–Sr2–O6	134.04
Sr2–N2#6	2.756	O8#4–Sr2–O6	78.67
Sr2–O7#4	2.765	O3–Sr2 –O1#3	89.65
Sr2–O5	3.005	O8#4–Sr2–O1#3	149.15
Sr2–C16#4	1.394	O3–Sr2–N2#6	148.41
Sr2–C9	3.005	O8–Sr2–N2#6	

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 x+1,y-1,z #3 -x+1,-y+1,-z+1

#4 x-1,y+1,z #5 -x,-y+2,-z+1 #6 -x+1,-y+1,-z+2

Table S5 Selected bond lengths (Å) and angles (deg.) for $[Ba_2(5AIP)_4Cl]_n$ (**2**)

Type of bond	Bond distance (Å)	Type of bond	Bond angle (deg.)
Ba1-O2	2.726	O(2)-Ba(1)-O(3)#2	118.98
Ba1-O6#1	2.747	O(6)#1-Ba(1)-O(3)#2	81.10
Ba1–O4#2	2.769	O(4)#2-Ba(1)-O(3)#2	46.25
Ba1–O7#3	2.785	O(7)#3-Ba(1)-O(3)#2	100.27
Ba1–O8#4	2.863	O(8)#4-Ba(1)-O(3)#2	155.17
Ba1–O3#2	2.865	O(2)-Ba(1)-O(1)	45.69
Ba1–O1	2.943	O(6)#1-Ba(1)-O(1)	142.20
Ba1–N	3.010	O(4)#2-Ba(1)-O(1)	115.43
Ba1–Cl	3.14076	O(7)#3-Ba(1)-O(1)	94.18
Ba1-Ba2#6	4.2034	O(8)#4-Ba(1)-O(1)	67.44
Ba2–O1	2.642	O(3)#2-Ba(1)-O(1)	136.54
Ba2–O3#7	2.693	O(2)-Ba(1)-Cl(1)	108.83
Ba2–O5	2.753	N(1)#5-Ba(1)-Cl(1)	176.25
Ba2–O7#4	2.765	O(1)-Ba(2)-O(3)#7	139.01
Ba2–O5#7	2.8371	O(1)-Ba(2)-O(5)	79.23
Ba2–O8#3	2.8547	O(3)#7-Ba(2)-O(5)	80.36
Ba2–O6#7	2.869	O(1)-Ba(2)-O(7)#4	69.71
Ba2–Cl#1	3.25324	O(3)#7-Ba(2)-O(7)#4	146.45
Ba2–Ba2#7	4.6672	O(5)-Ba(2)-O(7)#4	130.11
Ba1–C1	3.194	O(1)-Ba(2)-O(5)#7	98.96
Ba2–C9	3.222	O(3)#7-Ba(2)-O(5)#7	105.02
N1–H1A	0.839	O(5)-Ba(2)-O(5)#7	66.80
N2–H1B	0.841	O(3)#7-Ba(2)-O(8)#3	82.03
N2–H2A	0.859	O(7)#4-Ba(2)-O(8)#3	66.84
N2–H2B	0.850	O(5)-Ba(2)-O(6)#7	106.44
N2–H2C	0.862	O(8)#3-Ba(2)-O(6)#7	73.08

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z #2 x-1,y+1,z #3 -x+1,-y+2,-z #4 x+1,y,z
#5 -x+2,-y+2,-z-1 #6 -x+2,-y+2,-z #7 -x+2,-y+1,-z
#8 x+1,y-1,z #9 x,y-1,z #10 x-1,y,z

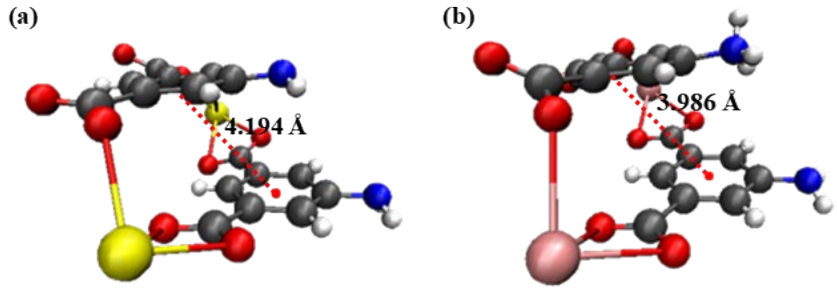


Figure S11 5-AIP ligands stacked in parallel offset fashion in complex (a) 1 and (b) 2

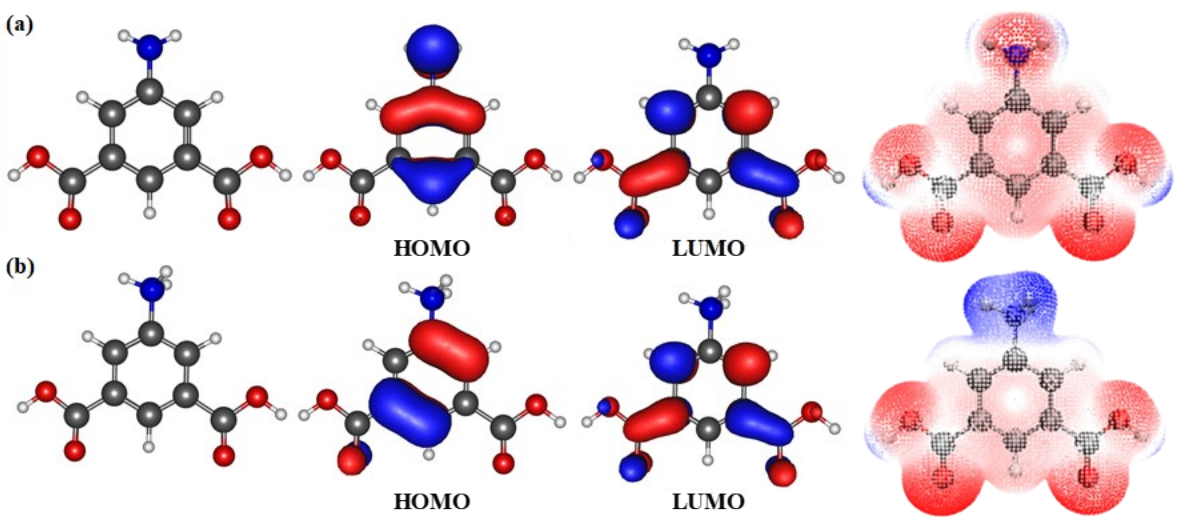
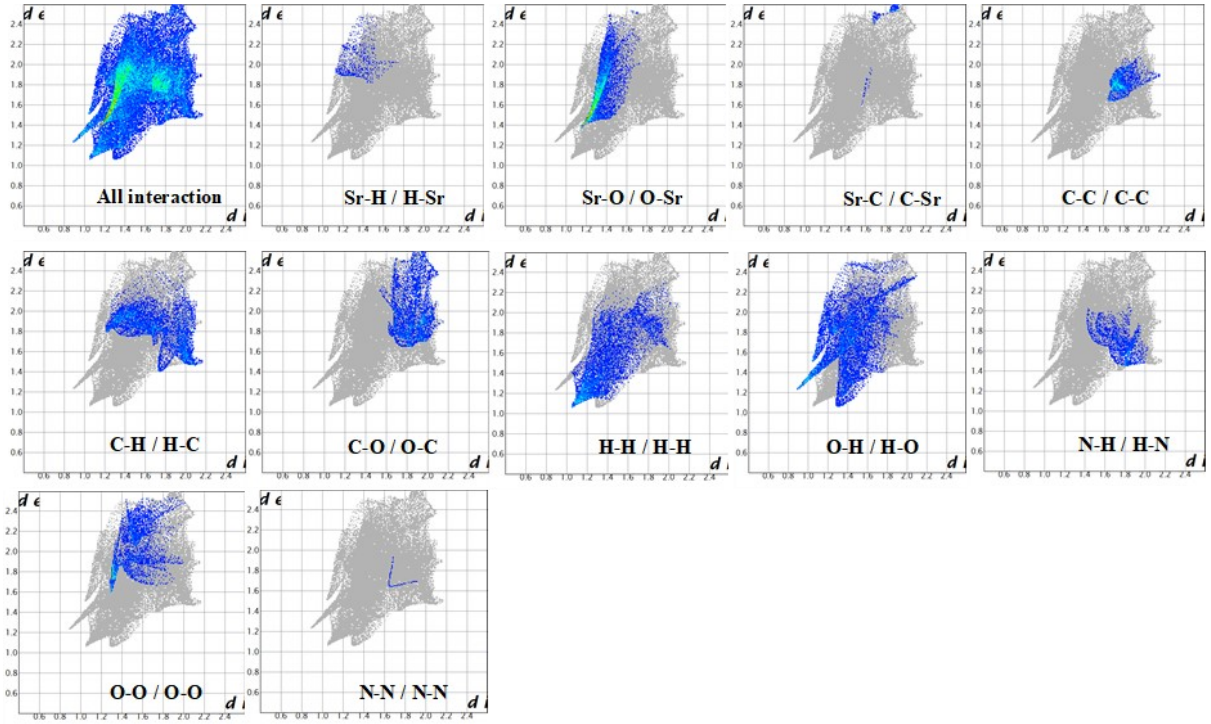
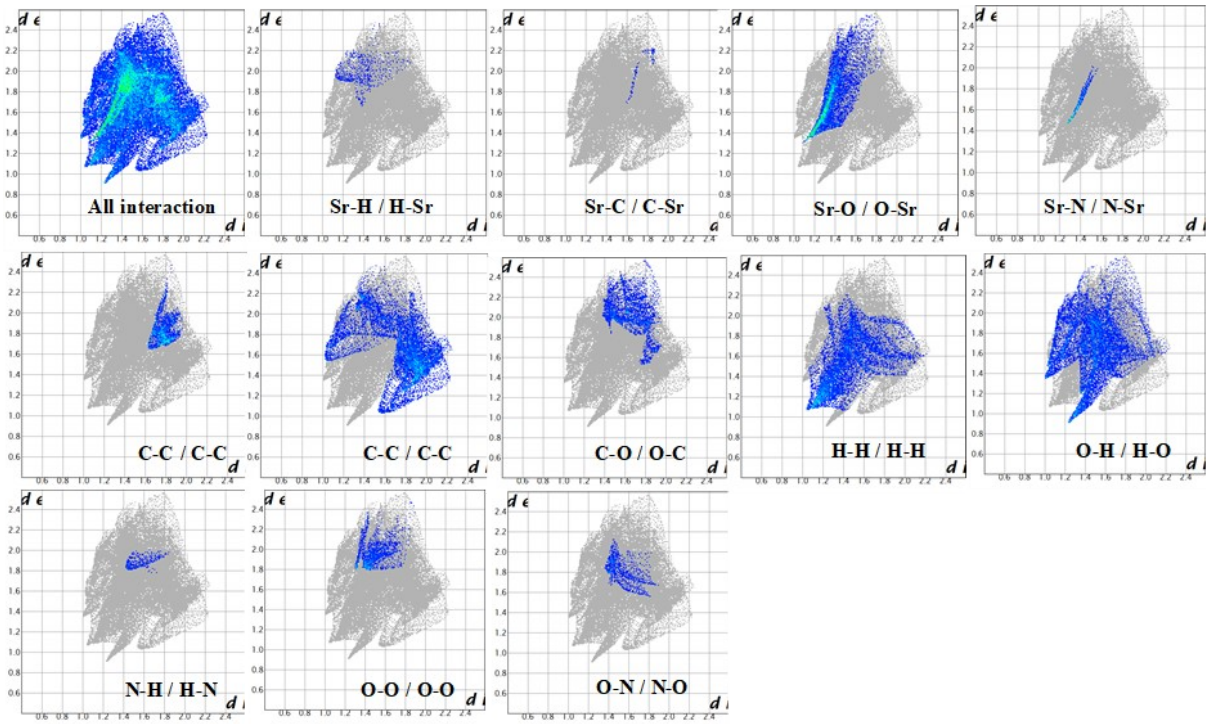


Figure S12 Optimized geometries, Frontier molecular orbitals and electrostatic potential mapping of (a) neutral and (b) protonated 5-aminoisophthalic acid.

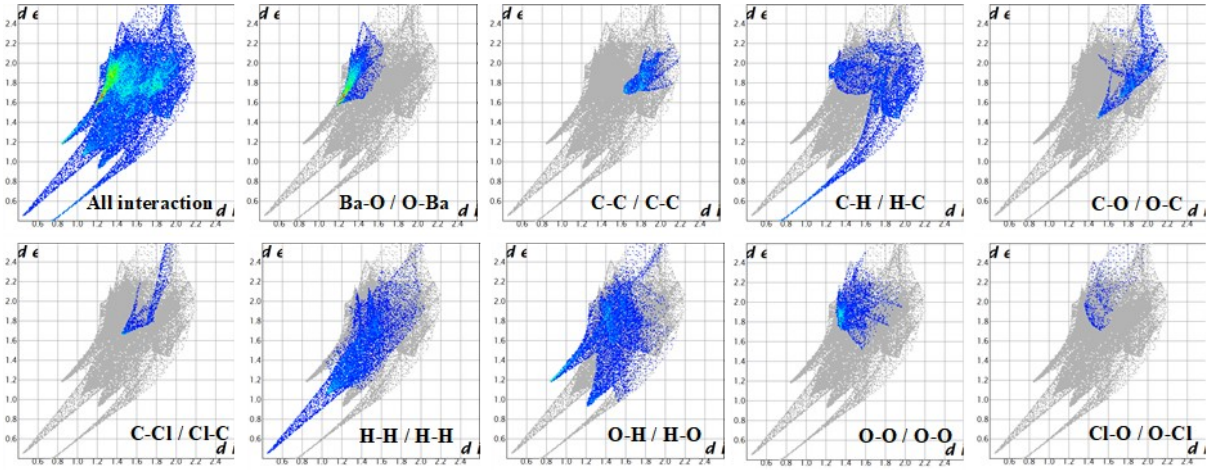
(a)


All interaction
Sr-H / H-Sr
Sr-O / O-Sr
Sr-C / C-Sr
C-C / C-C
C-H / H-C
C-O / O-C
H-H / H-H
O-H / H-O
N-H / H-N
O-O / O-O
N-N / N-N

(b)


All interaction
Sr-H / H-Sr
Sr-C / C-Sr
Sr-O / O-Sr
Sr-N / N-Sr
C-C / C-C
C-C / C-C
C-O / O-C
H-H / H-H
O-H / H-O
N-H / H-N
O-O / O-O
O-N / N-O

(c)



(d)

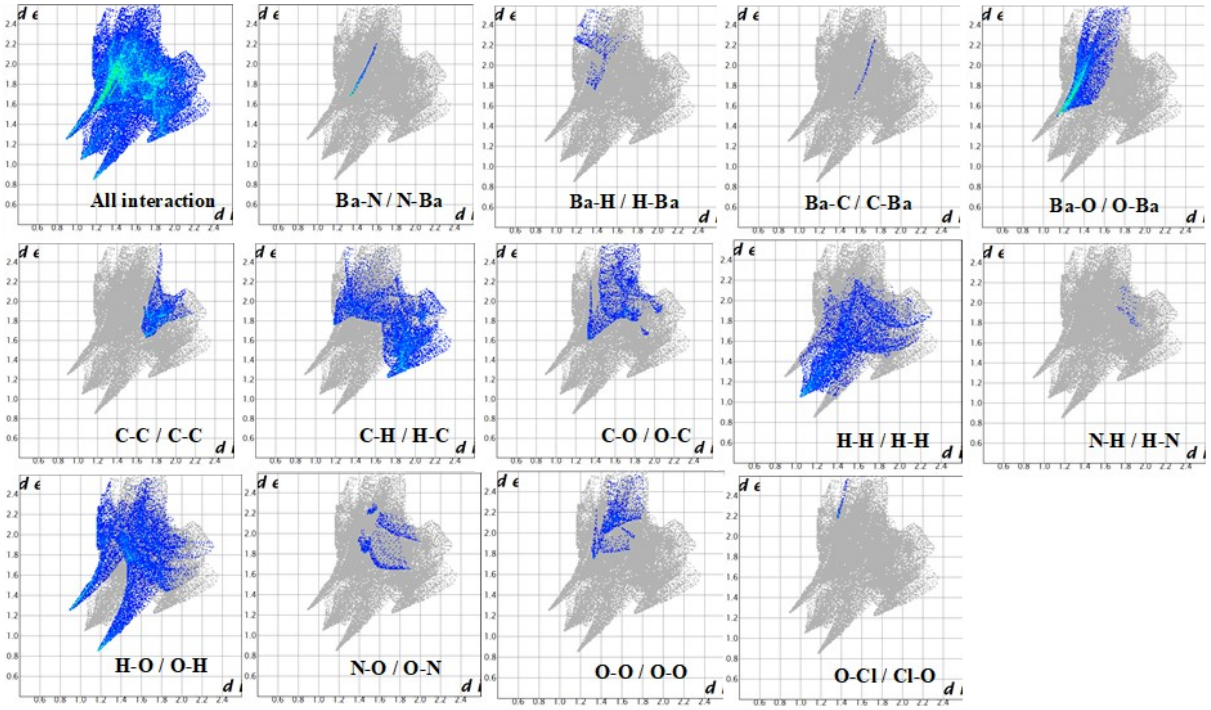


Figure S13 2D fingerprint plots of Hirshfeld surface of ligands coordinated (a) and uncoordinated (b) through amine in complex1 and coordinated (c) and protonated (d) ligands in complex 2, respectively.

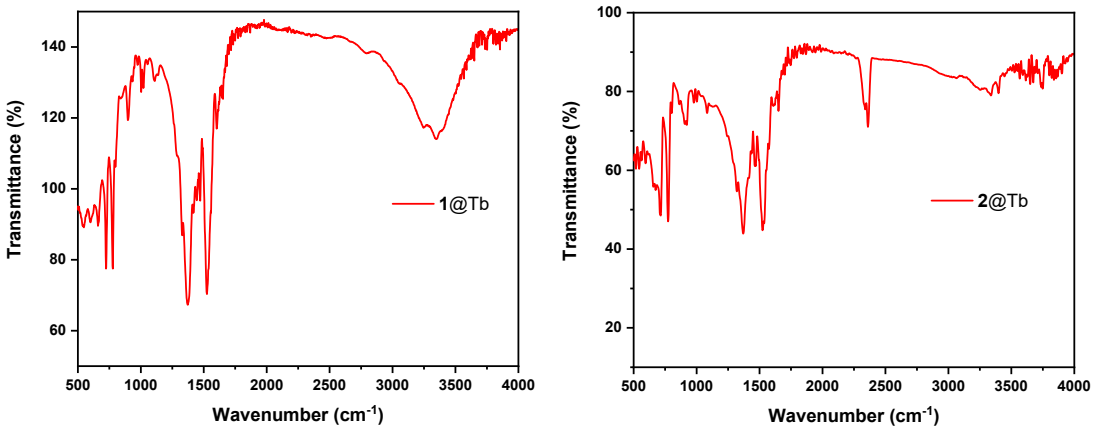


Figure S14 Infrared spectra of host Tb encapsulated complex **1** (left) and Tb encapsulated complex **2** (right).

Table S6 Lifetime decay information for **1**@Tb and **2**@Tb

System	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)	χ^2	τ_{avg} (μs)
1@Tb	85.04	244.12	426.49	1.02	306.21
2@Tb	24.33	65.98	197.19	1.03	70.39