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Cation Radii Induced Structural Variation in Fluorescent Alkaline Earth Networks Constructed from Tautomers of Nucleobases' Analogue †

Zhao-Peng Deng, Wei Kang, Zhi-Biao Zhu, Li-Hua Huo,* Hui Zhao and Shan Gao*

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Heilongjiang University, Harbin 150080, People's Republic of China

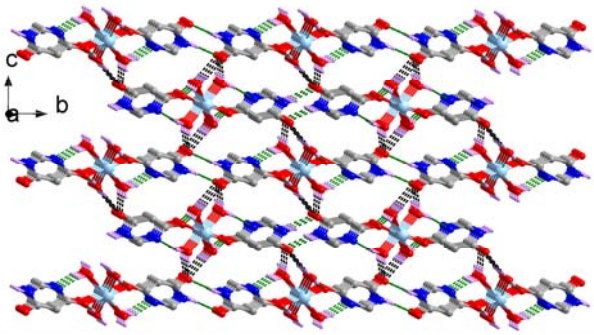

Fig. S1 3D supramolecular network of **1**.

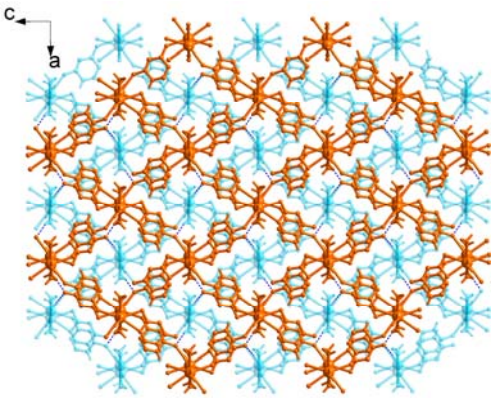

Fig. S2 3D framework linked by the interlayer hydrogen bonds with adjacent layers packed in an interlaced **ABAB** mode.

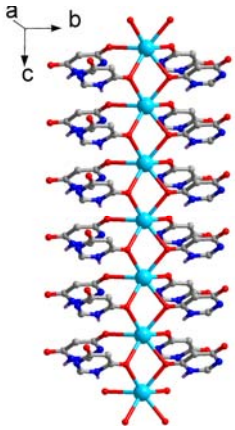

Fig. S3 Ball-and-stick representation of the infinite Ba-O rod.

Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns for solid samples of **1-4** are measured at room temperature as illustrated in Fig. S4. The patterns of complexes **1-3** are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding samples. However, the slightly mismatch between the powder diffraction data and the simulated pattern for complex **4** indicates the existence of very small amount of adherent impurity in the solid-state sample.

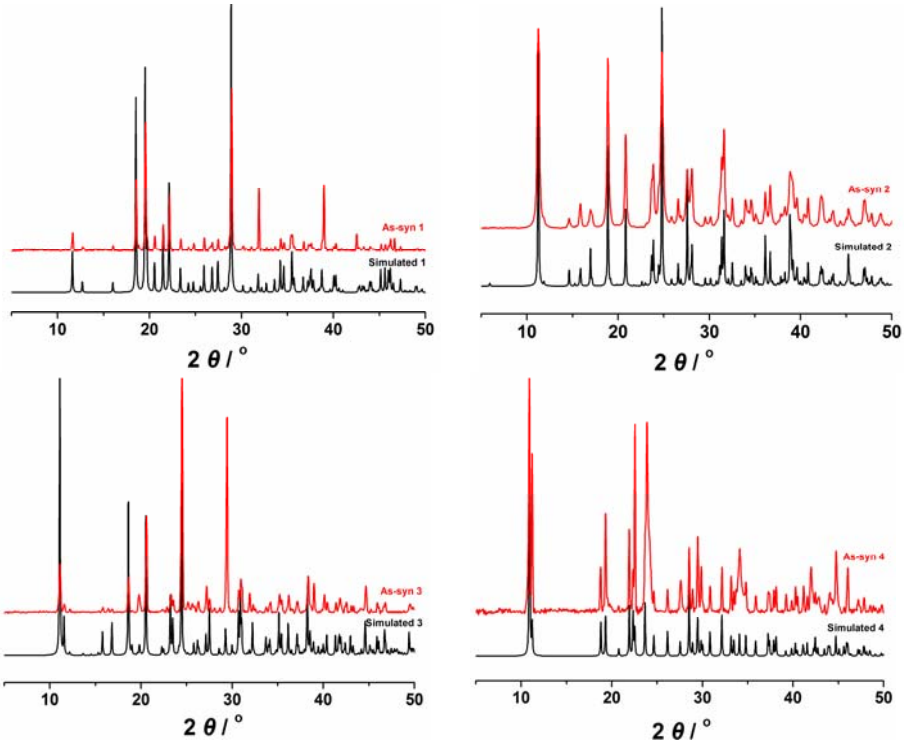

Fig. S4 PXRD patterns for complexes **1-4**.

Thermogravimetric analysis

To examine the thermal stability of the complexes, in this study, their stabilities were analyzed on crystalline samples by thermogravimetric analyses (TGA) from 30 to 900 °C at a rate of 10 °C min^{-1}, under N_2 atmosphere. As shown in Fig. S5, the TGA curve indicates that complex **1** loses the coordinated water molecules between 102-184 °C with the observed weight loss of 23.07% (calcd 22.62%). The next weight loss in the temperature range 280-847 °C is due to the decomposition of organic components. The residue has a composition of MgO (obsd 12.47%, calcd 12.65%). Complexes **2** and **3** have the similar formula except for the difference of metal cation, which result in the similar weight loss during the decomposition. The first weight losses between 90-315 °C for complex **2** and 110-320 °C for complex **3** corresponds to the release of free and coordinated water molecules (obsd 21.11%, calcd 21.55% for **2**; obsd 18.33%, calcd 18.87% for **3**). Then, the weight losses are continuously with the decomposing of organic components till, leaving the residue of CaO (obsd 16.46%, calcd 16.77%) for complex **2** and SrO (obsd 27.36%, calcd 27.14%) for complex **3**. Complex **4** loses the uncoordinated and coordinated water molecules before 177 °C with the observed weight loss of 13.03% (calcd 13.07%). Then, the organic components are decomposed progressively up to 595 °C, and the remaining weight of 37.58% corresponds to the percentage (calcd 37.08%) of the Ba and O components, BaO.

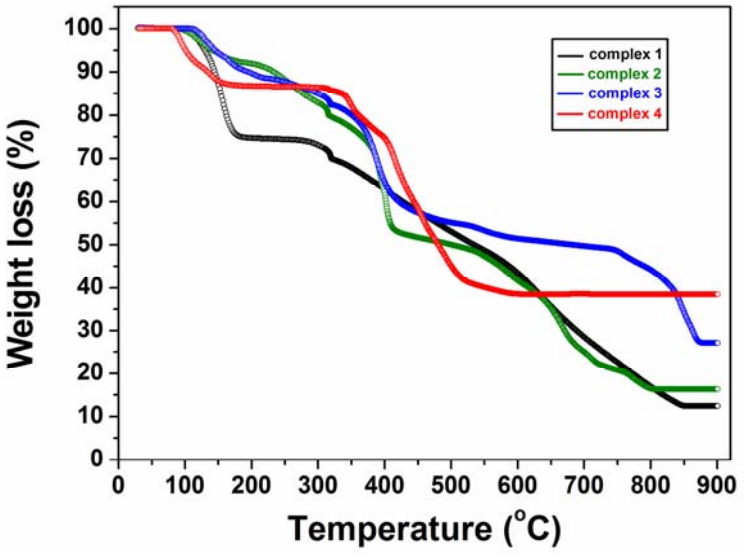

Fig. S5 TG curves of complexes **1-4**.

UV Spectra

UV spectra for ligand H_2DHP and complexes **1-4** in aqueous solution (10^{-3} M) are measured at room temperature. As illustrated in Fig. S6, H_2DHP and complexes **1-4** exhibit the same absorption band at 252 nm, which can be assigned to the π-π* transitions.

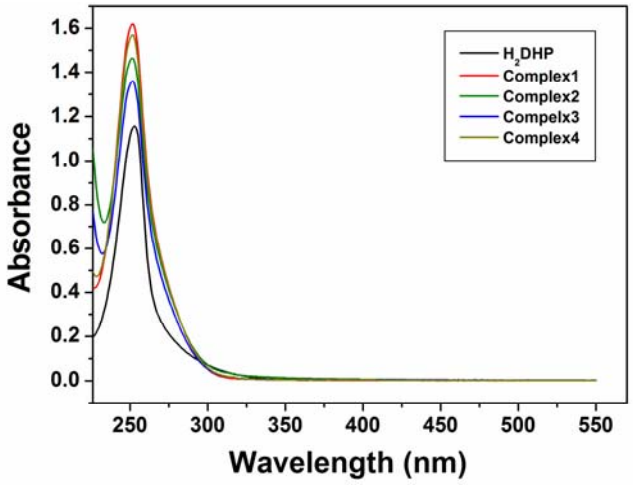

Fig. S6 UV spectra of ligand H_2DHP andcomplexes **1-4**.

Table S1. Crystallographic Data of Complexes **1-4**

	1	**2**	**3**	**4**
formula	$C_8H_{14}N_4O_8Mg$	$C_8H_{14}N_4O_8Ca$	$C_8H_{14}N_4O_8Sr$	$C_8H_{12}N_4O_7Ba$
fw	318.54	334.31	381.85	413.56
space group	$P2_1/c$	$Pcca$	$Pbca$	Cm
a/Å	5.1545(10)	14.347(3)	12.169(2)	9.5261(6)
b/Å	13.940(3)	14.902(3)	14.549(3)	15.7700(9)
c/Å	9.1871(18)	12.099(2)	15.315(3)	4.3128(2)
α/°	90.00	90.00	90.00	90.00
β/°	98.45(3)	90.00	90.00	97.767(2)
γ/°	90.00	90.00	90.00	90.00
V/Å^3	652.9(2)	2586.9(9)	2711.3(9)	641.95(6)
Z	2	8	8	2
D_c/g m^{-3}	1.620	1.717	1.871	2.139
μ /mm^{-1}	0.185	0.535	4.024	3.133
F(000)	332	1392	1536	400
reflections collected	6244	23744	18149	3127
unique reflections	1494	2953	3022	1329
parameters	112	220	220	113
R (int)	0.0281	0.0325	0.0528	0.0325
GOF on F^2	1.038	1.047	1.100	1.091
final R indices	$R_1 = 0.0347$	$R_1 = 0.0395$	$R_1 = 0.0450$	$R_1 = 0.0207$
$[I \geq 2\sigma(I)]$	$wR_2 = 0.0844$	$wR_2 = 0.0994$	$wR_2 = 0.0801$	$wR_2 = 0.0486$

Table S2 Selected Bond Distances (Å) for Complexes **1**-**4**[a]

Complex **1**			
Mg(1)-O(1W)^{i}	2.0442(11)	Mg(1)-O(2W)	2.0901(13)
Mg(1)-O(1W)	2.0442(11)	Mg(1)-O(1)	2.1169(10)
Mg(1)-O(2W)^{i}	2.0901(13)	Mg(1)-O(1)^{i}	2.1169(10)
Complex **2**			
Ca(1)-O(1W)	2.3925(16)	Ca(1)-O(2W)	2.4846(14)
Ca(1)-O(3)	2.4034(13)	Ca(1)-O(4)^{i}	2.5421(13)
Ca(1)-O(1)	2.4602(14)	Ca(1)-O(3W)^{ii}	2.5860(13)
Ca(1)-O(3W)	2.4715(13)	Ca(1)-N(1)	2.6954(16)
Complex **3**			
Sr(1)-O(1W)	2.533(3)	Sr(1)-O(3W)	2.612(3)
Sr(1)-O(1)	2.560(4)	Sr(1)-O(4)^{i}	2.670(3)
Sr(1)-O(3)	2.583(6)	Sr(1)-O(3W)^{ii}	2.706(3)
Sr(1)-O(2W)	2.591(3)	Sr(1)-N(1)	2.711(4)
Complex **4**			
Ba(1)-O(1W)	2.781(7)	Ba(1)-O(1)^{i}	2.828(4)
Ba(1)-O(2W)^{i}	2.792(5)	Ba(1)-O(2W)	2.872(6)
Ba(1)-O(1)	2.793(4)	Ba(1)-O(2)^{iv}	2.880(4)
Ba(1)-O(1)^{ii}	2.793(4)	Ba(1)-O(2)^{v}	2.880(4)
Ba(1)-O(1)^{iii}	2.828(4)		

[a] Symmetry Codes: For **1**: i, -x,-y+1,-z+1; For **2**: i, x,-y+2,z+1/2; ii, -x+1,y,-z+3/2; For **3**: i, x+1/2,y,-z+1/2; ii, -x+1,-y+1,-z+1; For **4**: i, x,y,z-1; ii, x,-y+1,z; iii, x,-y+1,z-1; iv, x+1/2,-y+3/2,z; v, x+1/2,y-1/2,z.

Table S3 Selected Hydrogen Bond Parameters for Complexes **1**-**4**[a]

D-H...A	d(H...A) /Å	d(D...A) /Å	<(DHA)/[o]
	Complex **1**		
O(1W)-H(1WA)...N(1)[i]	1.867(10)	2.6783(17)	157(2)
O(1W)-H(1WB)...O(2)[ii]	1.843(19)	2.6958(16)	174(2)
O(2W)-H(2WA)...O(1)[iii]	1.900(10)	2.7525(16)	174(2)
O(2W)-H(2WB)...O(2)[iv]	2.040(11)	2.8615(17)	162.8(17)
N(2)-H(2A)...O(2)[v]	1.98	2.7981(16)	159.8
	Complex **2**		
O(1W)-H(1WA)...O(4W)[iv]	1.967(12)	2.804(2)	168(3)
O(1W)-H(1WB)...O(2)[v]	2.014(12)	2.8218(19)	162(2)
O(2W)-H(2WA)...O(4)[vi]	1.993(10)	2.8431(18)	171(2)
O(2W)-H(2WB)...O(2)[vii]	2.005(10)	2.8542(19)	175(2)
O(3W)-H(3WA)...O(2)[viii]	2.085(14)	2.8185(17)	145.1(16)
O(3W)-H(3WB)...N(3)[ii]	1.876(10)	2.7191(19)	170(2)
O(3W)-H(3WB)...O(3)[ii]	2.564(19)	3.0057(18)	113.4(16)
O(4W)-H(4WA)...O(4)[i]	2.134(11)	2.959(2)	163(2)
O(4W)-H(4WB)...O(2)[viii]	2.051(13)	2.859(2)	162(2)
N(2)-H(2A)...O(1)[ix]	1.93	2.776(2)	169.7
N(4)-H(4A)...O(3)[iii]	1.80	2.6472(19)	166.3
	Complex **3**		
N(2)-H(2A)...O(1)[iv]	1.80	2.653(6)	170.4
N(4)-H(4A)...O(3)[iii]	1.77	2.617(8)	169.7
O(3W)-H(3W1)...O(2)[v]	1.94(3)	2.728(5)	154(6)
O(3W)-H(3W2)...N(3)[ii]	1.98(5)	2.821(7)	172(6)
O(1W)-H(1W1)...O(4W)	1.93(5)	2.770(6)	176(6)
O(4W)-H(4W1)...O(4)[vi]	2.63(8)	3.062(8)	113(8)
O(4W)-H(4W2)...O(2)[vii]	1.98(4)	2.734(8)	147(7)
O(2W)-H(2W1)...N(3)	2.53(6)	3.072(7)	122(6)
O(2W)-H(2W2)...O(4)[vi]	2.00(4)	2.758(6)	148(7)
O(1W)-H(1W2)...O(2)[viii]	1.92(6)	2.749(6)	164(6)
	Complex **4**		
N(1)-H(1)...O(2)[viii]	1.85	2.703(6)	168.9
O(1W)-H(1W1)...O(3W)	1.85(11)	2.702(10)	178(14)

O(1W)-H(1W2)...O(3W)[i]	2.35(6)	3.148(13)	157(13)
O(2W)-H(2W)...N(2)[iv]	2.06(2)	2.885(5)	164(7)
O(3W)-H(3W1)...N(2)[ix]	2.07(13)	2.854(6)	153(25)
O(3W)-H(3W2)...N(2)[x]	2.004(19)	2.854(6)	177(28)

[a] Symmetry transformations used to generate equivalent atoms: (i) -x,-y+1,-z+1; (ii) -x+1,y+1/2,-z+1/2; (iii) -x+1,-y+1,-z+1; (iv) x,-y+1/2,z+1/2; (v) -x+1,-y,-z+1 for **1**; (i) x,-y+2,z+1/2; (ii) -x+1,y,-z+3/2; (iii) x,-y+2,z-1/2; (iv) -x+3/2,y,z-1/2; (v) -x+3/2,-y+1,z; (vi) -x+3/2,-y+2,z; (vii) x,-y+1,z-1/2; (viii) -x+1,-y+1,-z+2; (ix) x,-y+1,z+1/2 for **2**; (ii) -x+1,-y+1,-z+1; (iii) x-1/2,y,-z+1/2; (iv) x+1/2,y,-z+3/2; (v) -x+3/2,-y+1,z-1/2; (vi) x,-y+1/2,z+1/2; (vii) -x+1,y-1/2,-z+3/2; (viii) x,-y+1/2,z-1/2 for **3**; (i) x,y,z-1; (iv) x+1/2,-y+3/2,z; (viii) x+1/2,-y+3/2,z+1; (ix) x-1/2,-y+3/2,z; (x) x-1/2,y-1/2,z for **4**.