A series of coordination polymers constructed from *in situ* amidation ligands: syntheses, structures and luminescent properties

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Table S1 Selected bond lengths (Å) and angles (°) for compounds **1**-**4**.

Compound **1**			
Cu(1)-O(2)A	1.862(3)	C(1)-O(1)	1.249(5)
Cu(1)-N(2)	1.889(3)	C(8)-O(2)	1.282(4)
Cu(1)-O(1W)	2.516(3)	C(9)-O(3)	1.217(5)
Cu(1)-Cu(1)A	2.6291(13)	C(9)-O(4)	1.316(5)
C(1)-N(1)	1.330(5)	C(10)-O(6)	1.193(5)
C(8)-N(2)	1.322(4)	C(10)-O(5)	1.315(5)
N(1)-N(2)	1.406(4)		
O(2)A-Cu(1)-N(2)	168.75(12)	O(2)-C(8)-N(2)	120.8(3)
O(2)A-Cu(1)-O(1W)	103.15(12)	O(3)-C(9)-O(4)	123.4(4)
N(2)-Cu(1)-O(1W)	87.94(12)	O(6)-C(10)-O(5)	124.9(3)
O(1)-C(1)-N(1)	121.4(3)		
Compound **2**			
Fe(1)-O(4)D	2.017(6)	C(1)-O(1)	1.271(11)
Fe(1)-O(1)	2.120(6)	C(1)-N(1)	1.303(11)
Fe(1)-O(6)C	2.125(6)	C(8)-O(2)	1.260(11)
Fe(1)-O(5)E	2.150(6)	C(8)-N(2)	1.342(12)
Fe(1)-O(3W)	2.221(6)	C(9)-O(3)	1.257(11)
Fe(1)-N(1)	2.277(7)	C(9)-O(4)	1.266(11)
Fe(2)-O(3)D	2.018(6)	C(10)-O(6)	1.218(9)
Fe(2)-O(2W)	2.132(6)	C(10)-O(5)	1.219(10)
Fe(2)-O(3W)	2.289(6)	N(1)-N(2)	1.413(11)
O(1)-Fe(1)-O(6)C	93.9(2)	O(5)E-Fe(1)-O(3W)	83.1(2)
O(1)-Fe(1)-O(5)E	92.3(2)	O(5)E-Fe(1)-N(1)	96.7(2)
O(1)-Fe(1)-O(3W)	96.9(2)	O(6)C-Fe(1)-O(5)E	166.7(2)
O(1)-Fe(1)-N(1)	59.7(2)	O(6)C-Fe(1)-N(1)	96.6(2)
O(3)B-Fe(2)-O(3)D	180.000(1)	O(6)C-Fe(1)-O(3W)	84.4(2)
O(3)B-Fe(2)-O(2W)	90.6(3)	O(2W)A-Fe(2)-O(2W)	180.000(1)
O(3)D-Fe(2)-O(2W)	89.4(3)	O(2W)A-Fe(2)-O(3W)A	85.9(2)
O(3)B-Fe(2)-O(3W)	86.8(2)	O(2W)-Fe(2)-O(3W)A	94.1(2)
O(3)D-Fe(2)-O(3W)	93.2(2)	O(2W)-Fe(2)-O(3W)	85.9(2)
O(4)D-Fe(1)-O(1)	158.7(3)	O(3W)A-Fe(2)-O(3W)	180.000(2)
O(4)D-Fe(1)-O(6)C	91.1(3)	O(3W)-Fe(1)-N(1)	156.6(3)
O(4)D-Fe(1)-O(3W)	104.2(2)	O(3)-C(9)-O(4)	125.8(8)
O(4)D-Fe(1)-O(5)E	87.3(3)	O(6)-C(10)-O(5)	129.0(7)
O(4)D-Fe(1)-N(1)	99.2(3)		
Compound **3**			
Zn(1)-O(3)B	1.948(2)	C(1)-O(1)	1.309(4)
Zn(1)-O(1)	1.980(2)	C(4)-O(2)	1.249(4)
Zn(1)-N(5)	2.042(3)	C(5)-O(3)	1.292(4)
Zn(1)-O(1W)	2.103(3)	C(8)-O(4)	1.252(4)
C(1)-N(1)	1.303(4)	N(1)-N(2)	1.379(4)
C(4)-N(2)	1.328(4)	N(3)-N(4)	1.387(4)

C(5)-N(3)	1.318(4)	N(5)-N(5)A	1.446(5)
C(8)-N(4)	1.333(4)		
O(3)B-Zn(1)-O(1)	106.41(10)	N(5)-Zn(1)-O(1W)	98.65(11)
O(3)B-Zn(1)-N(5)	115.25(11)	N(1)-C(1)-O(1)	117.3(3)
O(1)-Zn(1)-N(5)	131.76(10)	O(2)-C(4)-N(2)	121.8(3)
O(3)B-Zn(1)-O(1W)	98.36(10)	O(3)-C(5)-N(3)	119.9(3)
O(1)-Zn(1)-O(1W)	98.26(10)	O(4)-C(8)-N(4)	121.4(3)
Compound **4**			
Cd(1)-O(18)	2.292(7)	C(27)-N(5)	1.302(14)
Cd(1)-O(17)	2.350(9)	C(28)-N(8)	1.383(17)
Cd(1)-N(9)	2.378(8)	C(36)-N(7)	1.334(15)
Cd(1)-O(1)	2.400(8)	C(1)-O(1)	1.279(15)
Cd(1)-N(10)	2.418(8)	C(5)-O(4)	1.223(14)
Cd(1)-O(8)	2.456(8)	C(5)-O(3)	1.266(14)
Cd(1)-O(7)	2.534(8)	C(9)-O(2)	1.309(13)
Cd(2)-O(19)	2.354(8)	C(10)-O(5)	1.289(15)
Cd(2)-O(20)	2.383(9)	C(14)-O(7)	1.268(14)
Cd(2)-N(12)	2.391(9)	C(14)-O(8)	1.285(13)
Cd(2)-O(10)A	2.399(8)	C(18)-O(6)	1.346(12)
Cd(2)-N(11)	2.418(8)	C(19)-O(10)	1.303(14)
Cd(2)-O(12)	2.452(8)	C(23)-O(12)	1.253(13)
Cd(2)-O(11)	2.514(9)	C(23)-O(11)	1.293(13)
C(1)-N(1)	1.363(15)	C(27)-O(9)	1.336(12)
C(9)-N(2)	1.304(14)	C(28)-O(14)	1.247(16)
C(10)-N(3)	1.351(16)	C(32)-O(16)	1.248(15)
C(18)-N(4)	1.317(14)	C(32)-O(15)	1.271(14)
C(19)-N(6)	1.349(15)	C(36)-O(13)	1.281(14)
O(18)-Cd(1)-O(17)	172.4(3)	N(12)-Cd(2)-N(11)	69.9(3)
O(18)-Cd(1)-N(9)	96.0(3)	O(10)A-Cd(2)-N(11)	74.9(3)
O(17)-Cd(1)-N(9)	87.8(4)	O(19)-Cd(2)-O(12)	90.5(3)
O(18)-Cd(1)-O(1)	100.4(3)	N(12)-Cd(2)-O(10)A	135.4(3)
O(17)-Cd(1)-O(1)	80.9(3)	O(19)-Cd(2)-N(11)	79.7(3)
N(9)-Cd(1)-O(1)	138.7(3)	O(20)-Cd(2)-O(12)	84.7(3)
O(18)-Cd(1)-N(10)	81.5(3)	N(12)-Cd(2)-O(12)	85.8(3)
O(17)-Cd(1)-N(10)	106.1(3)	O(10)A-Cd(2)-O(12)	132.8(3)
N(9)-Cd(1)-N(10)	69.0(3)	N(11)-Cd(2)-O(12)	152.3(3)
O(1)-Cd(1)-N(10)	76.3(3)	O(19)-Cd(2)-O(11)	83.4(3)
O(18)-Cd(1)-O(8)	81.1(3)	O(20)-Cd(2)-O(11)	92.1(3)
O(17)-Cd(1)-O(8)	91.7(3)	N(12)-Cd(2)-O(11)	139.1(3)
N(9)-Cd(1)-O(8)	138.5(3)	O(10)A-Cd(2)-O(11)	83.2(3)
O(1)-Cd(1)-O(8)	81.7(3)	N(11)-Cd(2)-O(11)	148.3(3)
N(10)-Cd(1)-O(8)	148.8(3)	O(12)-Cd(2)-O(11)	53.3(2)
O(18)-Cd(1)-O(7)	89.9(3)	O(1)-C(1)-N(1)	123.2(11)
O(17)-Cd(1)-O(7)	83.8(3)	O(4)-C(5)-O(3)	123.4(11)

N(9)-Cd(1)-O(7)	85.3(3)	N(2)-C(9)-O(2)	121.8(10)
O(1)-Cd(1)-O(7)	131.9(3)	O(5)-C(10)-N(3)	121.7(11)
N(10)-Cd(1)-O(7)	151.7(3)	O(7)-C(14)-O(8)	123.3(10)
O(8)-Cd(1)-O(7)	53.5(2)	N(4)-C(18)-O(6)	119.2(9)
O(19)-Cd(2)-O(20)	174.8(3)	O(10)-C(19)-N(6)	118.1(11)
O(19)-Cd(2)-N(12)	96.6(3)	O(12)-C(23)-O(11)	122.2(9)
O(20)-Cd(2)-N(12)	85.1(4)	N(5)-C(27)-O(9)	119.0(9)
O(19)-Cd(2)-O(10)A	103.2(3)	O(14)-C(28)-N(8)	120.5(12)
O(20)-Cd(2)-O(10)A	78.7(3)	O(16)-C(32)-O(15)	126.7(10)
O(20)-Cd(2)-N(11)	105.5(3)		

Symmetry code for **1**: A, 3-x, -y, 1-z

Symmetry codes for **2**: A, 1-x, 1-y, 1-z; B, 1-x, 1-y, 2-z; C, -x, -y, 2-z; D, x, y, -1+z; E, 1-x, -y, 2-z;

Symmetry codes for **3**: A, 1-x, 2-y, 1-z; B, 2-x, 1/2+y, 3/2-z;

Symmetry code for **4**: A, 1/2+x, -y, z;

Table S2 Selected hydrogen-bond parameters for compounds **1**-**4**.

D-H…A	*d* (D-H)(Å)	*d* (H…A)(Å)	*d* (D…A)(Å)	∠(D-H…A)(°)
Compound **1**				
N1-H1…O1W	0.94(6)	2.08(6)	2.807(4)	134(5)
O4-H4…O2WD	0.82	1.84	2.651(5)	172.2
O5-H5…O1B	0.82	1.79	2.604(4)	173.6
O1W-H1WA…O2WE	0.85	2.47	3.190(5)	143.3
O1W-H1WA…O3E	0.85	2.50	3.094(5)	127.6
O1W-H1WB…O6F	0.85	2.10	2.820(4)	142.1
O2W-H2A…O5G	0.89(6)	2.46(6)	3.111(5)	130(4)
O2W-H2B…O1B	0.86(8)	1.93(8)	2.764(5)	162(8)
Compound **2**				
O3W-H3WB…O1WA	0.85	1.84	2.678(10)	166.1
O1W-H1WA…O1D	0.85	1.98	2.813(9)	167.1
O1W-H1WB…O2G	0.85	2.17	2.942(10)	151.0
Compound **3**				
O3W-H3WA…O1WG	0.85	2.27	3.048(4)	152.9
O3W-H3WB…O2H	0.85	1.89	2.719(3)	162.0
O2W-H2WB…O3W	0.85	2.11	2.954(4)	170.9
O2W-H2WA…O4I	0.85	1.87	2.717(3)	175.4
O1W-H1WB…O1F	0.85	1.93	2.718(3)	154.1
O1W-H1WA…O2WA	0.85	1.86	2.711(4)	176.3
N2-H2…O4E	0.86	1.95	2.804(4)	175.5
N4-H4…O2D	0.86	1.98	2.838(4)	176.3
Compound **4**				
O13-H13…N4	0.82	1.93	2.730(12)	166.1
N1-H1A…O8	0.86	1.89	2.726(13)	162.3
O6-H6…N7	0.82	1.99	2.803(12)	169.9
O19-H19B…O16	0.85	1.89	2.744(12)	176.7
O2-H2…N5C	0.82	1.91	2.729(12)	174.0
O18-H18B…O5C	0.85	2.01	2.856(11)	176.6
N8-H8A…O15C	0.86	1.93	2.786(14)	177.8
O18-H18A…O3E	0.85	1.93	2.775(12)	177.1
O9-H9…N2E	0.82	1.98	2.795(11)	174.7
O19-H19A…O14E	0.85	2.01	2.856(12)	177.0
O17-H17A…O3H	0.85	2.34	3.181(14)	170.2
O17-H17B…O5G	0.85	2.07	2.910(12)	169.6
N3-H3A…O4D	0.86	1.94	2.799(14)	177.8
N6-H6A…O11F	0.86	1.92	2.754(13)	164.6
O20-H20B…O15I	0.85	2.21	2.951(14)	145.8

Symmetry codes for compound **1**: B, x, 1+y, z; D, -x, 1-y, -z ; E, 1+x, -1+y, z; F, 2-x, -y, 1-z; G, 1-x, 1-y, -z;

Symmetry codes for compound **2**: A, 1-x, 1-y, 1-z; D, x, y, -1+z; G, -x, -y, -1+z;

Symmetry codes for compound **3**: A, 1-x, 2-y, 1-z; B, 2-x, 1/2+y, 3/2-z; D, 1+x, y, 1+z; E, -1+x, y, -1+z; F, 2-x, 2-y, 1-z; G, -1+x, y, z; H, x, y, 1+z; I, x, 3/2-y, 1/2+z;

Symmetry codes for compound **4**: C, -1/2+x, 1-y, z; D, 1+x, y, z; E, 1/2+x, 1-y, z; F, -1/2+x, -y, z; G, -1/2+x, 2-y, z.; H, 1/2+x, 2-y, z; I, x, -1+y, z.

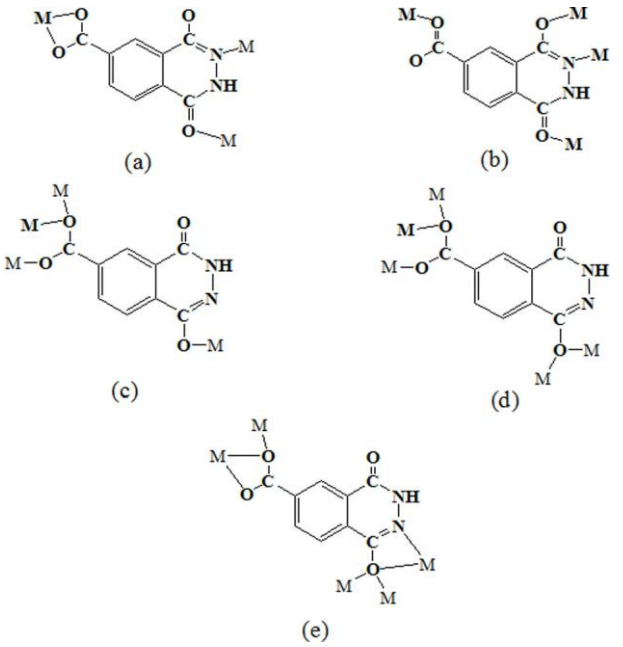
Table S3 Selected π-π interactions geometry for **1-4** (The plane-to-plane distance (*d*), the dihedral angles (*α*), the centroid-centroid distance (*c*) and the displacement angle between the planes (*θ*)).

π-π interactions	*d* (Å)	*α* (°)	*c* (Å)	*θ* (°)
Compound **1**				
H_3bbch-H_3bbch (inter-molecular)	3.3490(15)	0	3.596(2)	21.38
Cg(1) [1] → Cg(1) [2756.01]				
Compound **2**				
Hbbch-Hbbch (inter-molecular)	3.216(3)	1.0(4)	3.386(5)	18.25
Cg6 [1] → Cg5 [2557.01]				
Hbbch-Hbbch (inter-molecular)	3.215(3)	1.0(4)	3.526(5)	24.22
Cg(6) [1] → Cg(5) [2657.01]				
Compound **3**				
H_2bbh-H_2bbh (inter-layers)	3.2279(15)	4	3.512(2)	23.23
Cg(4) [1] → Cg(4) [4564.01]				
H_2bbh-H_2bbh (inter-layers)	3.2377(15)	4	3.513(2)	22.82
Cg(4) [1] → Cg(4) [4565.01]				
Compound **4**				
H_2bch-H_2bch	3.467(5)	1.8(5)	3.978(7)	29.38
(inter-molecular in part A)				
Cg(10) [2] → Cg(11) [4465.02]				
H_2bch-H_2bch	3.531(5)	1.8(5)	3.888(7)	24.71
(inter-molecular in part A)				
Cg(10) [2] → Cg(11) [4475.02]				
2,2'-bpy-2,2'-bpy	3.522(5)	2.8(6)	3.590(8)	11.17
(inter-molecular between part A and part C)				
Cg(3) [1] → Cg(9) [2664.02]				
H_2bch-H_2bch	3.518(5)	0.2(5)	3.889(7)	25.25
(inter-molecular between part B and part C)				
Cg(4) [1] → Cg(15) [1555.03]				
H_2bch-H_2bch	3.580(5)	0.2(5)	3.966(7)	25.48
(inter-molecular between part B and part C)				
Cg(4) [1] → Cg(15) [1545.03]				

Cg(1) in compound **1**: the 6-membered ring containing N1N2C8C7C2C1.
Cg(5) in compound **2**: the 6-membered ring containing N1N2C8C7C2C1.
Cg(6) in compound **2**: the 6-membered ring containing C2C3C4C5C6C7.
Cg(4) in compound **3**: the 6-membered ring containing C2C3C9C6C7C10.
Cg(3) in compound **4**: the 6-membered ring containing N12C52C53C54C55C56.
Cg(4) in compound **4**: the 6-membered ring containing C20C21C22C24C25C26.
Cg(9) in compound **4**: the 6-membered ring containing N10C42C43C44C45C46.
Cg(10) in compound **4**: the 6-membered ring containing C2C3C4C6C7C8.
Cg(11) in compound **3**: the 6-membered ring containing C11C12C13C15C16C17.
Cg(15) in compound **3**: the 6-membered ring containing C29C30C31C33C34C35.

Table S4 The C-O and C-N distances of the acylhydrazidate ring in compounds **1**-**4**.

compound	*d*(C-O) (Å)	*d*(C=O) (Å)	*d*(C=N) (Å)	*d*(C-N) (Å)
1	C8-O2=1.282(4)	C1-O1=1.249(5)	C8-N2=1.322(4)	C1-N1=1.330(5)
2	C1-O1=1.271(11)	C8-O2=1.260(11)	C1-N1=1.303(11)	C8-N2=1.342(12)
3	C1-O1=1.309(4)	C4-O2=1.249(4)	C1-N1=1.303(4)	C4-N2=1.328(4)
	C5-O3=1.292(4)	C8-O4=1.252(4)	C5-N3=1.318(4)	C8-N4=1.333(4)
4	C9-O2=1.309(13)	C1-O1=1.279(15)	C9-N2=1.304(14)	C1-N1=1.363(15)
	C18-O6=1.346(12)	C10-O5=1.289(15)	C18-N4=1.317(14)	C10-N3=1.351(16)
	C27-O9=1.336(12)	C19-O10=1.303(14)	C27-N5=1.302(14)	C19-N6=1.349(15)
	C36-O13=1.281(14)	C28-O14=1.247(16)	C36-N7=1.334(15)	C28-N8=1.383(17)



Scheme S1 The five kinds of coordination modes of H_3bch found by Xu.[7a,7e]

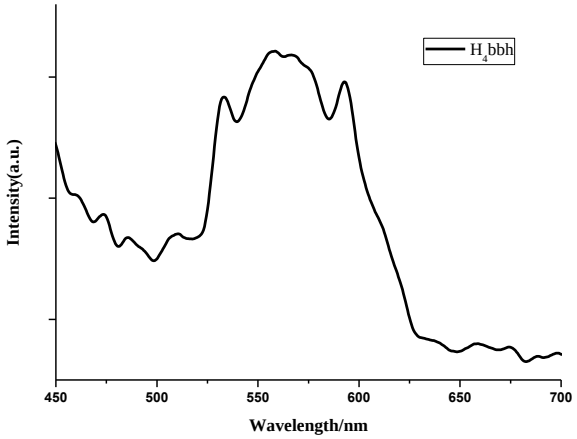


Fig. S1 The fluorescent emissions of H_4bbh (λ_{ex} = 394 nm) in solid state at room temperature.