Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic supplementary information

An unusual lamellar framework constructed from a tetracarboxylatocalix[4]arene that presents highly efficient metal-ion exchange

Table S1a Selected bond distances (Å) and angles (deg) for **1**.

Zn(1)-O(4)$^{\#1}$	1.994(2)	Zn(1)-O(1)	2.039(3)
Zn(1)-O(17)$^{\#2}$	2.051(2)	Zn(1)-O(5)$^{\#3}$	2.054(2)
Zn(1)-O(17)$^{\#1}$	2.122(2)	Zn(2)-O(17)	1.944(2)
Zn(2)-O(6)$^{\#4}$	1.962(2)	Zn(2)-O(7)$^{\#1}$	1.980(3)
Zn(2)-O(3)	1.991(2)	Zn(2)-O(8)$^{\#1}$	2.410(3)
O(4)$^{\#1}$-Zn(1)-O(1)	101.81(11)	O(4)$^{\#1}$-Zn(1)-O(17)$^{\#2}$	102.77(10)
O(1)-Zn(1)-O(17)$^{\#2}$	154.52(10)	O(4)$^{\#1}$-Zn(1)-O(5)$^{\#3}$	94.17(9)
O(1)-Zn(1)-O(5)$^{\#3}$	91.53(10)	O(17)$^{\#2}$-Zn(1)-O(5)$^{\#3}$	93.30(9)
O(4)$^{\#1}$-Zn(1)-O(17)$^{\#1}$	99.37(9)	O(1)-Zn(1)-O(17)$^{\#1}$	90.20(10)
O(17)$^{\#2}$-Zn(1)-O(17)$^{\#1}$	79.28(9)	O(5)$^{\#3}$-Zn(1)-O(17)$^{\#1}$	165.70(9)
O(17)-Zn(2)-O(6)$^{\#4}$	106.87(9)	O(17)-Zn(2)-O(7)$^{\#1}$	128.09(11)
O(6)$^{\#4}$-Zn(2)-O(7)$^{\#1}$	112.64(11)	O(17)-Zn(2)-O(3)	101.52(9)
O(6)$^{\#4}$-Zn(2)-O(3)	100.17(9)	O(7)$^{\#1}$-Zn(2)-O(3)	103.14(10)
O(17)-Zn(2)-O(8)$^{\#1}$	89.32(10)	O(6)$^{\#4}$-Zn(2)-O(8)$^{\#1}$	91.94(12)
O(7)$^{\#1}$-Zn(2)-O(8)$^{\#1}$	57.80(10)	O(3)-Zn(2)-O(8)$^{\#1}$	160.52(10)

Table S1b Hydrogen bonds for **1** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(17)-H(1A)...O(2)$^{\#1}$	0.826(19)	2.56(4)	2.987(3)	113(3)
N(1)-H(1B)...O(12)$^{\#2}$	0.851(19)	2.22(3)	2.969(4)	146(4)
N(1)-H(1C)...O(2)	0.872(19)	1.86(2)	2.720(4)	169(5)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+2, -y+1, -z+1; $^{\#2}$ x, y+1, z; $^{\#3}$ x+1, y+1, z; $^{\#4}$ x+1, y, z.

Table S2a Selected bond distances (Å) and angles (deg) for **2**.

Zn(1)-O(6)$^{\#1}$	1.962(3)	Zn(1)-O(2)	1.999(3)
Zn(1)-O(1W)	2.008(3)	Zn(1)-O(3)$^{\#2}$	2.032(4)

O(6)$^{\#1}$-Zn(1)-O(2)	120.08(13)	O(6)$^{\#1}$-Zn(1)-O(1W)	106.63(14)
O(2)-Zn(1)-O(1W)	101.45(14)	O(6)$^{\#1}$-Zn(1)-O(3)$^{\#2}$	131.05(17)
O(2)-Zn(1)-O(3)$^{\#2}$	95.58(16)	O(1W)-Zn(1)-O(3)$^{\#2}$	96.65(14)

Table S2b Hydrogen bonds for **2** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1A)...O(2)$^{\#4}$	0.834(19)	2.23(3)	2.763(5)	122(3)
O(1W)-H(1B)...O(6W)	0.873(19)	1.83(2)	2.699(5)	170(6)
N(1)-H(1C)...O(3W)	0.873(10)	1.84(3)	2.641(8)	152(5)
N(1)-H(1F)...O(1)	0.859(10)	2.08(3)	2.891(6)	157(6)
N(2)-H(2A)...O(7)$^{\#5}$	0.853(9)	2.42(5)	2.953(6)	122(4)
N(2)-H(2B)...O(2W)	0.853(9)	1.941(12)	2.791(6)	174(4)
N(2)-H(2D)...O(1)$^{\#5}$	0.852(10)	2.39(5)	2.952(6)	124(5)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, y+1, z; $^{\#2}$ -x+1, -y+1, -z; $^{\#3}$ x, y-1, z; $^{\#4}$ -x+1, -y+2, -z; $^{\#5}$ -x+2, -y+1, -z.

Table S3a Selected bond distances (Å) and angles (deg) for **3**.

Cd(1)-O(5)$^{\#1}$	2.236(7)	Cd(1)-O(6)$^{\#2}$	2.250(6)
Cd(1)-O(3)	2.288(6)	Cd(1)-O(4)$^{\#3}$	2.323(5)
Cd(1)-O(7)$^{\#4}$	2.402(6)	Cd(1)-O(8)$^{\#4}$	2.434(7)
Cd(2)-O(1)	2.148(8)	Cd(2)-O(1W)	2.247(7)
Cd(2)-O(9)	2.286(9)	Cd(2)-O(7)$^{\#1}$	2.322(6)
Cd(2)-O(10)	2.334(8)	Cd(2)-O(18)$^{\#1}$	2.418(5)
O(5)$^{\#1}$-Cd(1)-O(6)$^{\#2}$	147.9(3)	O(5)$^{\#1}$-Cd(1)-O(3)	84.7(2)
O(6)$^{\#2}$-Cd(1)-O(3)	84.3(2)	O(5)$^{\#1}$-Cd(1)-O(4)$^{\#3}$	87.7(2)
O(6)$^{\#2}$-Cd(1)-O(4)$^{\#3}$	86.4(2)	O(3)-Cd(1)-O(4)$^{\#3}$	149.0(2)
O(5)$^{\#1}$-Cd(1)-O(7)$^{\#4}$	109.9(3)	O(6)$^{\#2}$-Cd(1)-O(7)$^{\#4}$	100.4(2)
O(3)-Cd(1)-O(7)$^{\#4}$	129.4(2)	O(4)$^{\#3}$-Cd(1)-O(7)$^{\#4}$	81.4(2)
O(5)$^{\#1}$-Cd(1)-O(8)$^{\#4}$	94.6(3)	O(6)$^{\#2}$-Cd(1)-O(8)$^{\#4}$	112.5(3)
O(3)-Cd(1)-O(8)$^{\#4}$	78.5(2)	O(4)$^{\#3}$-Cd(1)-O(8)$^{\#4}$	132.1(2)
O(7)$^{\#4}$-Cd(1)-O(8)$^{\#4}$	52.9(2)	O(1)-Cd(2)-O(1W)	119.1(3)
O(1)-Cd(2)-O(9)	83.9(3)	O(1W)-Cd(2)-O(9)	94.6(3)
O(1)-Cd(2)-O(7)$^{\#1}$	151.6(3)	O(1W)-Cd(2)-O(7)$^{\#1}$	86.6(2)
O(9)-Cd(2)-O(7)$^{\#1}$	81.9(3)	O(1)-Cd(2)-O(10)	110.8(3)
O(1W)-Cd(2)-O(10)	85.1(3)	O(9)-Cd(2)-O(10)	163.3(3)
O(7)$^{\#1}$-Cd(2)-O(10)	81.4(3)	O(1)-Cd(2)-O(18)$^{\#1}$	88.6(3)
O(1W)-Cd(2)-O(18)$^{\#1}$	152.0(2)	O(9)-Cd(2)-O(18)$^{\#1}$	91.7(3)

O(7)$^{\#1}$-Cd(2)-O(18)$^{\#1}$	67.4(2)	O(10)-Cd(2)-O(18)$^{\#1}$	81.1(2)

Table S3b Hydrogen bonds for **3** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1B)...O(15)$^{\#5}$	0.88(2)	1.98(5)	2.785(8)	153(10)
O(1W)-H(1A)...O(4)$^{\#5}$	0.88(2)	1.89(6)	2.675(9)	148(10)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x-1, y, z; $^{\#2}$ -x+2, -y, -z+1; $^{\#3}$ -x+1, -y, -z+1; $^{\#4}$ -x+1, -y+1, -z+1; $^{\#5}$ x-1, y+1, z.

Fig. S1 The coordination environment of tetranuclear Zn(II) cluster in **1**.

Fig. S2 The coordination environment of tetranuclear Cd(II) cluster in **3**.

Fig. S3 PXRD patterns for the simulated (black) and experimental (blue) of **2** and **3** (the patterns suggest the phase purity since the experimental data dovetail well with the simulative ones).

Fig. S4 The amplifying photographs of **1** (left) and Cu^{2+}-exchanged sample **1a** (right).

We can only obtain the cell parameters of **1a** because of the efflorescence of the samples. Nevertheless, by comparing the data, we can see that the cell parameters of **1a** were similar with those of **1**.

The cell parameters of **1**: a = 12.2409(6) Å, b = 13.5072(7) Å, c = 20.2897(14) Å, α = 103.942(10) °, β = 100.864(8) °, γ = 93.222(5) °, V = 3179.3(3) $Å^3$.

The cell parameters of **1a**: a = 12.2528(10) Å, b = 13.4684(12) Å, c = 20.2323(19) Å, α = 103.888(8) °, β = 100.909(7) °, γ = 93.292(7) °, V = 3164.1(5) $Å^3$.

Fig. S5 Luminescence decay curves for H_4TCC4A and compounds **1**-**3** (the black circles represent experimental data, and the solid red lines represent fitting results).