Supporting Information

Fluorescent Heterometallic MOFs: Tunable Framework Charges and Application for Explosive Detection

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1. XRD, IR and TGA curves of 1, 2, 3, and 5

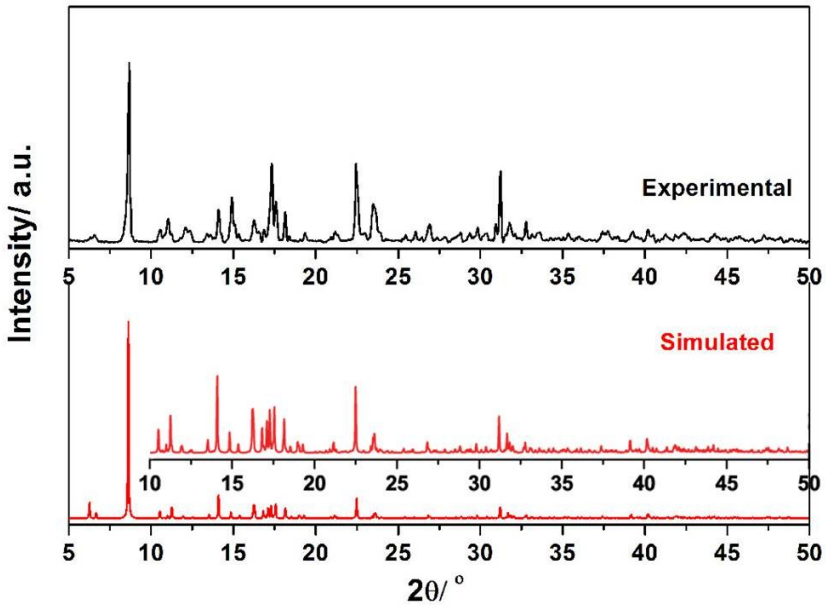

Fig. S1 Simulated and experimental powder XRD patterns of compound **1**. Inset: the simulated powder XRD pattern from 10 to 50 degree of compound **1**.

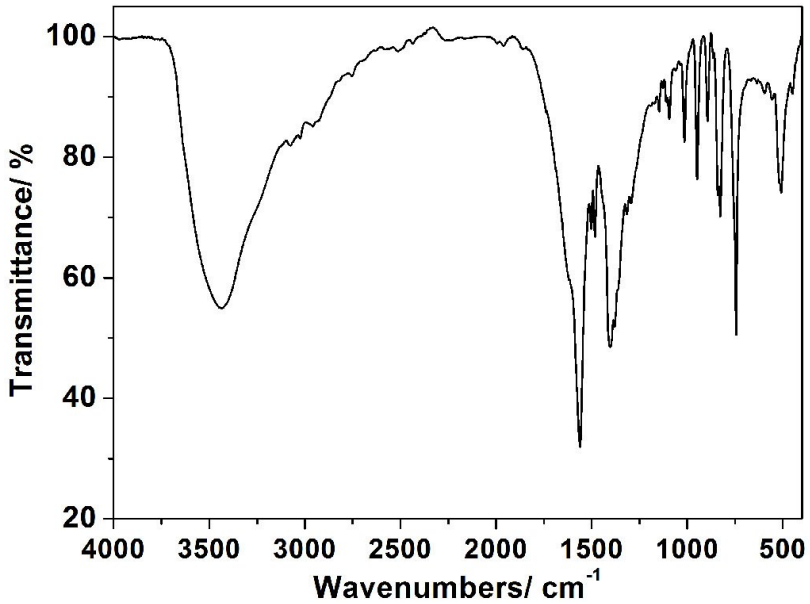

Fig. S2 IR spectra of compound **1**. IR (KBr pellets, cm^{-1}): 3435 (m), 1560 (s), 1502 (m), 1482 (m), 1404 (s), 1379 (m), 1147 (w), 1093 (m), 1015 (m), 948 (m), 825 (m), 744 (m), 509 (m) cm^{-1}.

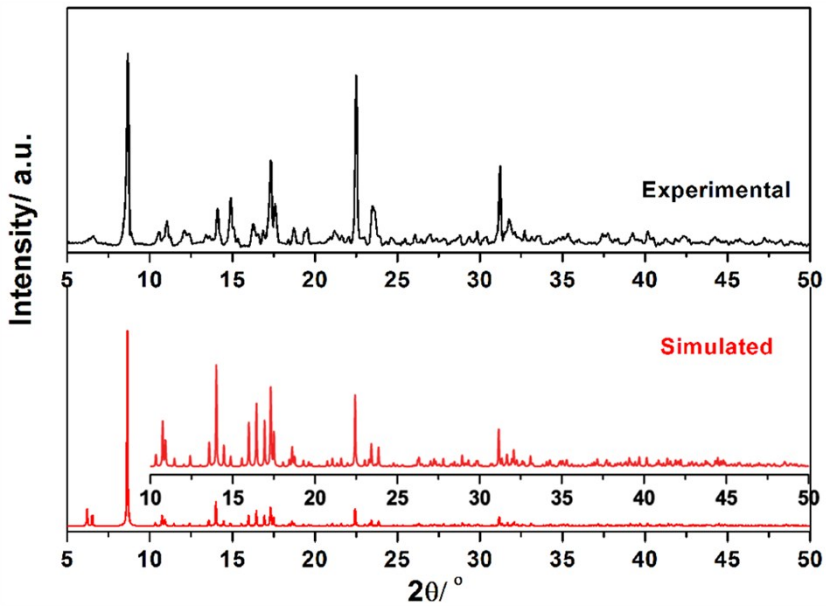

Fig. S3 Simulated and experimental powder XRD patterns of compound **2**. Inset: the simulated powder XRD pattern from 10 to 50 degree of compound **2**.

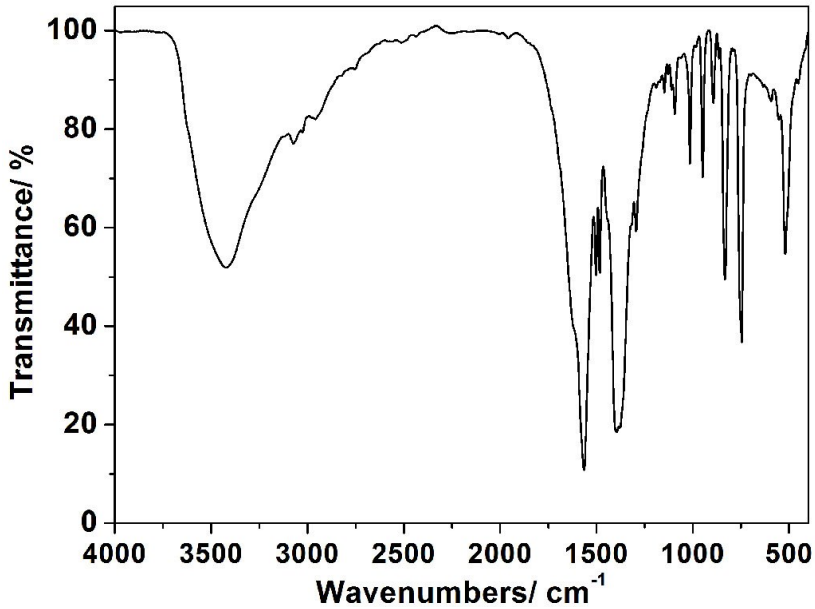

Fig. S4 IR spectra of compound **2**. IR (KBr pellets, cm^{-1}): 3422 (m), 1564 (s), 1502 (m), 1483 (m), 1396 (s), 1294 (m), 1148 (w), 1093 (m), 1015 (m), 948 (m), 833 (m), 746 (m), 520 (m) cm^{-1}.

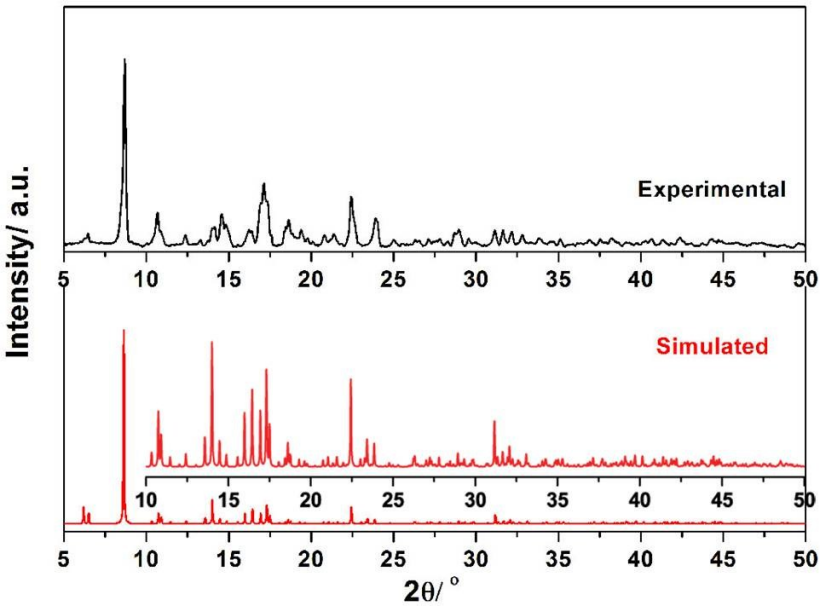

Fig. S5 Simulated and experimental powder XRD patterns of compound **3**. Inset: the simulated powder XRD pattern from 10 to 50 degree of compound **3**.

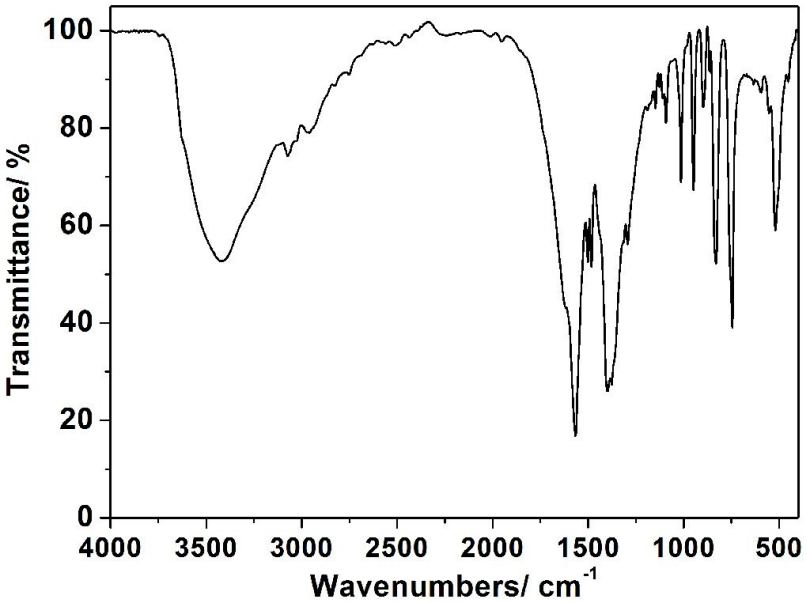

Fig. S6 IR spectra of compound **3**. IR (KBr pellets, cm^{-1}): 3420 (m), 1566 (s), 1501 (m), 1483 (m), 1399 (s), 1293 (m), 1127 (w), 1094 (m), 1014 (m), 948 (m), 830 (m), 745 (m), 519 (m) cm^{-1}.

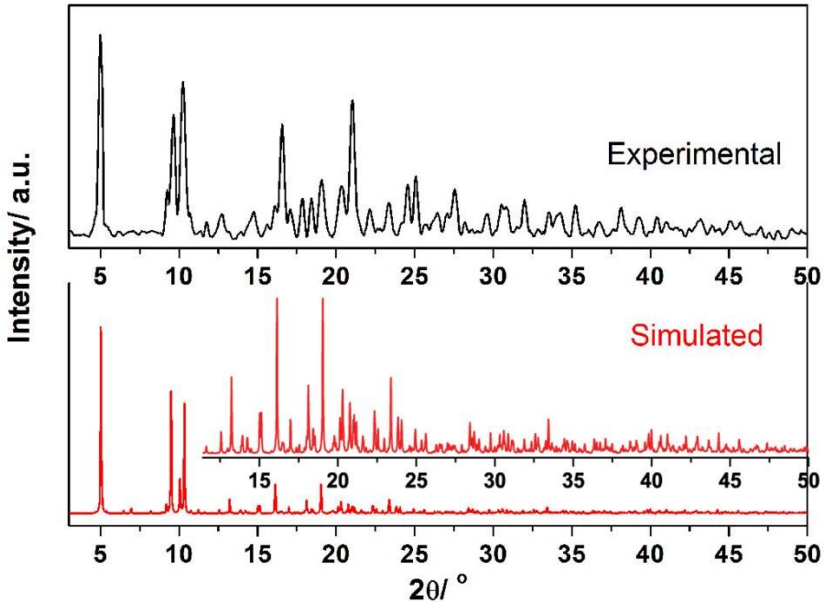

Fig. S7 Simulated and experimental powder XRD patterns of compound **5**. Inset: the simulated powder XRD pattern from 11 to 50 degree of compound **5**.

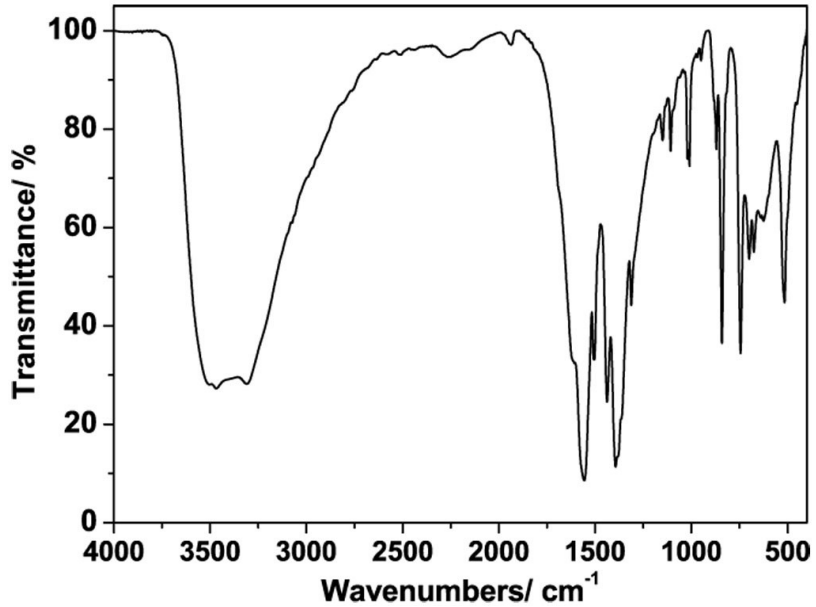

Fig. S8 IR spectra of compound **5**. IR (KBr pellets, cm^{-1}): 3468 (m), 3309 (m), 1555 (s), 1503 (m), 1437 (m), 1394 (s), 1312 (m), 1149 (w), 1108 (w), 1020 (m), 1109 (m), 841 (m), 744 (m), 519 (m) cm^{-1}.

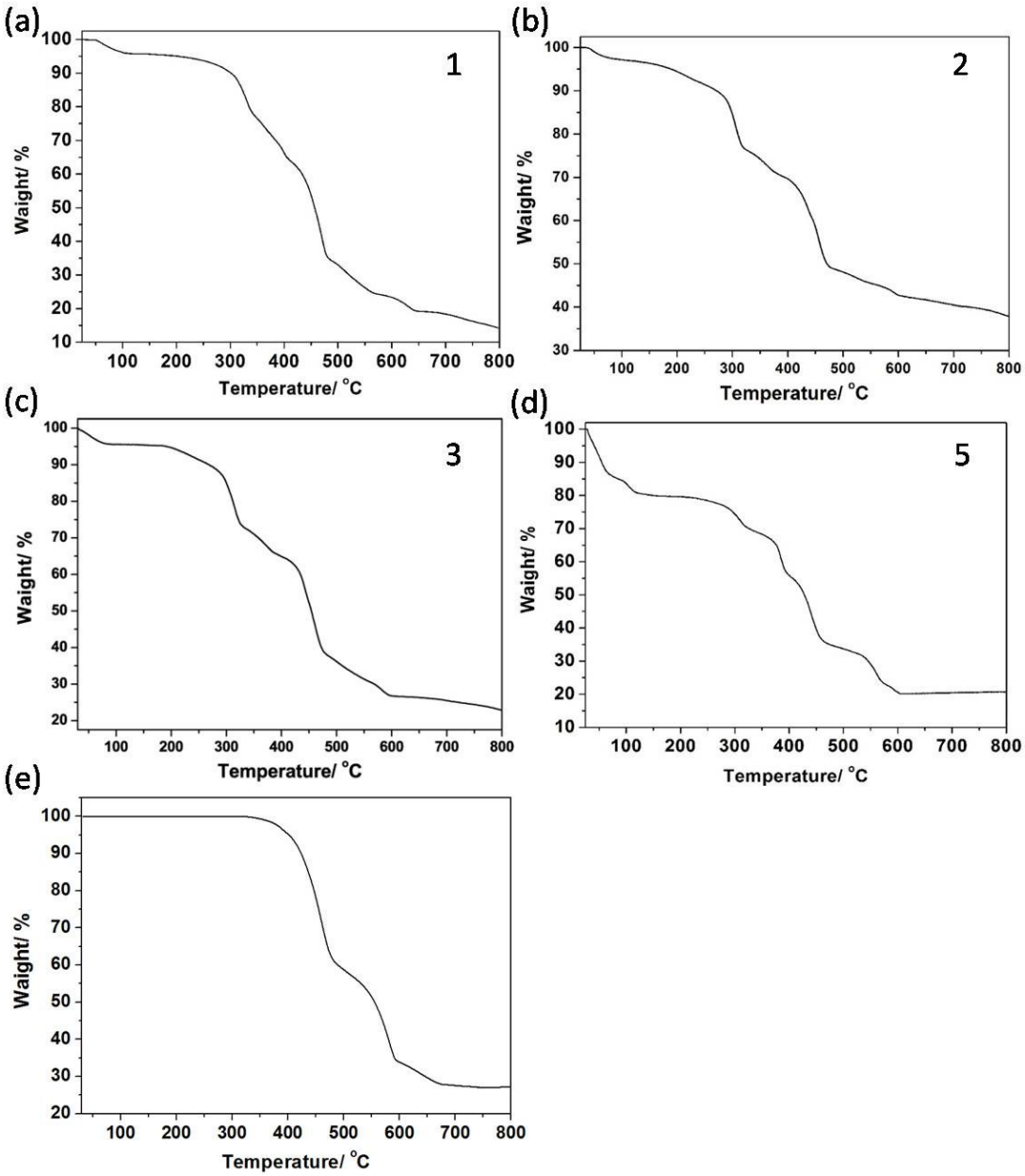

Fig. S9 Thermo-gravimetric analyses of **1**, **2**, **3**, **5**, and **5'** (degassed 5).

2. Structural illustration and selected bond lengths and angles of 1-5

Table S1 Crystal Data and Structure Refinements for Compound **1-5**[a, b]

	1	**2**	**3**	**4**	**5**
formula	$C_{104}H_{66}O_{51}N_2Na_6Cd_6$	$C_{96}H_{48}O_{51}Cd_6Na_4K_2$	$C_{63}H_{49}O_{29}N_4Cd_3K_3$	$C_{104}H_{66}O_{57}N_2Mg_6Cd_6$	$C_{76}H_{67}O_{35}N_5Ca_2Cd_4$
fw	2971.93	2861.90	1780.56	3075.85	2140.11
crystal system	monoclinic	monoclinic	Monoclinic	monoclinic	orthorhombic
space group	*C2/c*	*C*2/*c*	*C*2/*c*	*C2/c*	*Pna*2$_1$
a, Å	18.4148(9)	18.9895(13)	19.2145(17)	18.5166(7)	19.9990(11)
b, Å	29.5574(15)	28.481(2)	26.4088(17)	29.4652(8)	18.6284(11)
c, Å	16.3155(8)	16.9587(18)	17.7174(12)	16.3850(4)	35.123(0)
α, °	90.00	90.00	90.00	90.00	90.00
β, °	119.2690(10)	119.896(2)	118.431(2)	119.388(3)	90.00
γ, °	90.00	90.00	90.00	90.00	90.00
V, Å^3	7746.7(7)	7951.5(11)	7906.1(10)	7789.2(4)	13084.9(13)
Z	2	2	4	2	4
T, K	298	100	296	298	296
D_c, g cm^{-3}	1.274	1.195	1.496	1.311	1.086
μ, mm^{-1}	0.896	0.916	1.035	7.366	0.778
F(000)	2932.0	2804.0	3552.0	3040	4280.0
2*ϑ* [°]	2.76-50.02	6 -50.02	3.004-55.2	11.22-145.52	4.24-52.24
GOF on F^2	1.023	1.048	1.072	1.031	1.050
$R_1{}^a$ [I > 2σ(I)]	0.0405	0.0549	0.0697	0.0624	0.0736
$wR_2{}^b$[I > 2σ(I)]	0.1127	0.1456	0.1629	0.1628	0.1774
R_1(all data)	0.0551	0.0899	0.0979	0.0836	0.0830
wR_2(all data)	0.1233	0.1707	0.1934	0.1829	0.1819

[a] $R_1 = \Sigma||F_o| - |Fc||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

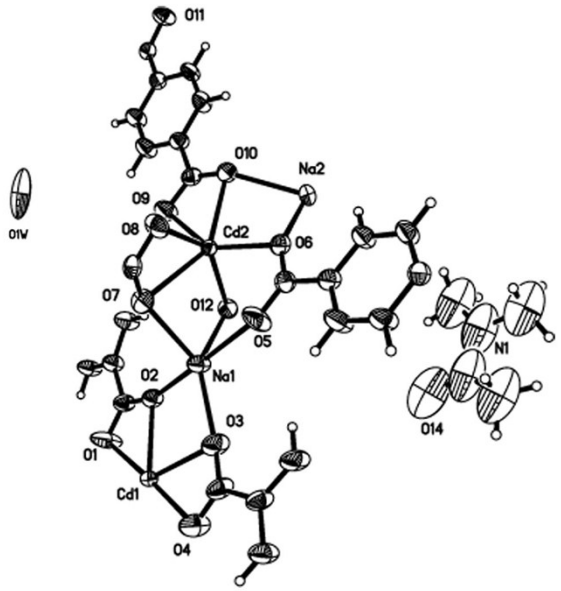

Fig. S10 ORTEP plot of the asymmetric unit of compound **1**, showing the labelling scheme and the 50% probability displacement ellipsoid.

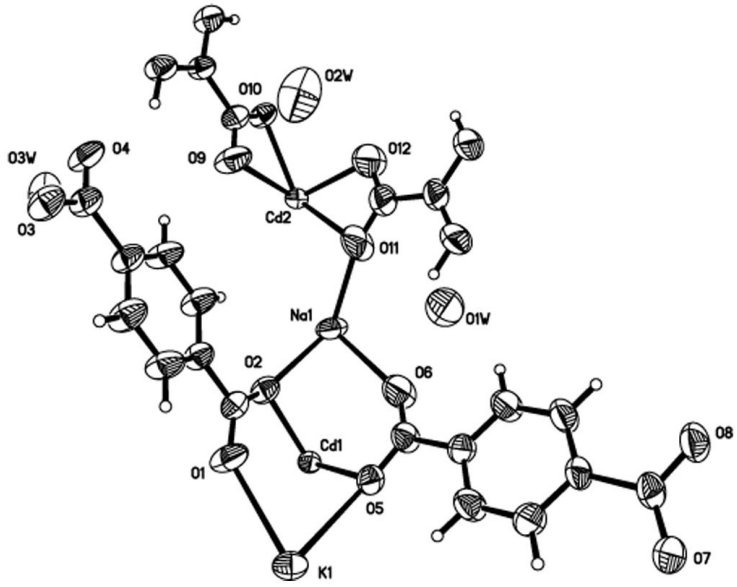

Fig. S11 ORTEP plot of the asymmetric unit of compound **2**, showing the labelling scheme and the 50% probability displacement ellipsoid.

Table S2 The selected bond lengths [Å] and angles [°] of compound **1**[a].

Cd(1)-O(2)	2.329(3)	Cd(2)-O(12)	2.224(3)
Cd(1)-O(2)#1	2.329(3)	Cd(2)-O(7)	2.509(3)
Cd(1)-O(4)	2.320(4)	Cd(2)-O(9)	2.314(3)
Cd(1)-O(4)#1	2.320(4)	O(7)-Na(1)	2.374(4)
Cd(1)-O(1)	2.451(4)	O(3)-Na(1)	2.262(4)
Cd(1)-O(1)#1	2.451(4)	O(12)-Na(1)	2.385(4)
Cd(1)-O(3)#1	2.549(4)	O(2)-Na(1)	2.352(3)
Cd(1)-O(3)	2.549(4)	O(5)-Na(1)	2.448(4)
Cd(2)-O(6)	2.229(3)	O(6)-Na(2)	2.479(4)
Cd(2)-O(8)	2.284(3)	O(10)-Na(2)	2.431(3)
Cd(2)-O(10)	2.430(3)	O(11)-Na(2)#3	2.520(3)
O(2)#1-Cd(1)-O(2)	133.04(16)	O(8)-Cd(2)-O(9)	94.07(14)
O(2)-Cd(1)-O(1)	54.50(11)	O(10)-Cd(2)-O(7)	145.12(11)
O(2)#1-Cd(1)-O(1)#1	54.50(11)	O(12)-Cd(2)-O(6)	94.92(11)
O(2)#1-Cd(1)-O(1)	89.69(12)	O(12)-Cd(2)-O(8)	139.76(12)
O(2)-Cd(1)-O(1)#1	89.69(12)	O(12)-Cd(2)-O(10)	117.55(12)
O(2)-Cd(1)-O(3)#1	127.65(11)	O(12)-Cd(2)-O(7)	85.87(11)
O(2)-Cd(1)-O(3)	76.43(11)	O(12)-Cd(2)-O(9)	98.41(13)
O(2)#1-Cd(1)-O(3)	127.65(11)	O(9)-Cd(2)-O(10)	55.03(11)
O(2)#1-Cd(1)-O(3)#1	76.43(11)	O(9)-Cd(2)-O(7)	98.57(12)
O(4)#1-Cd(1)-O(2)	85.73(12)	O(12)-Na(1)-O(5)	81.65(13)
O(4)#1-Cd(1)-O(2)#1	129.42(12)	O(2)-Na(1)-O(12)	91.53(12)
O(4)-Cd(1)-O(2)	129.42(12)	O(2)-Na(1)-O(5)	173.05(15)
O(4)-Cd(1)-O(2)#1	85.73(12)	O(2)-Na(1)-O(7)	97.31(13)
O(4)#1-Cd(1)-O(4)	90.6(2)	O(7)-Na(1)-O(12)	85.52(12)
O(4)-Cd(1)-O(1)	175.41(13)	O(7)-Na(1)-O(5)	83.55(14)
O(4)-Cd(1)-O(1)#1	92.17(18)	O(3)-Na(1)-O(12)	135.18(16)
O(4)#1-Cd(1)-O(1)	92.17(18)	O(3)-Na(1)-O(2)	81.83(12)
O(4)#1-Cd(1)-O(1)#1	175.41(13)	O(3)-Na(1)-O(5)	102.05(14)
O(4)#1-Cd(1)-O(3)	86.44(15)	O(3)-Na(1)-O(7)	139.22(16)
O(4)-Cd(1)-O(3)#1	86.44(15)	O(6)#9-Na(2)-O(6)	85.14(16)
O(4)-Cd(1)-O(3)	52.98(12)	O(6)#9-Na(2)-O(11)#2	165.11(14)
O(4)#1-Cd(1)-O(3)#1	52.98(12)	O(6)#9-Na(2)-O(11)#3	80.73(11)
O(1)#1-Cd(1)-O(1)	85.3(2)	O(6)-Na(2)-O(11)#3	165.11(14)
O(1)#1-Cd(1)-O(3)#1	130.84(11)	O(6)-Na(2)-O(11)#2	80.73(11)
O(1)-Cd(1)-O(3)#1	92.33(14)	O(10)-Na(2)-O(6)#9	101.19(12)
O(1)#1-Cd(1)-O(3)	92.33(14)	O(10)#9-Na(2)-O(6)#9	82.80(11)
O(1)-Cd(1)-O(3)	130.84(11)	O(10)#9-Na(2)-O(6)	101.19(12)
O(3)#1-Cd(1)-O(3)	123.64(18)	O(10)-Na(2)-O(6)	82.80(11)
O(6)-Cd(2)-O(8)	97.67(13)	O(10)#9-Na(2)-O(10)	174.7(2)
O(6)-Cd(2)-O(10)	88.24(11)	O(10)#9-Na(2)-O(11)#3	81.74(12)
O(6)-Cd(2)-O(7)	116.76(12)	O(10)-Na(2)-O(11)#3	95.32(12)
O(6)-Cd(2)-O(9)	143.00(12)	O(10)-Na(2)-O(11)#2	81.74(12)
O(8)-Cd(2)-O(10)	100.94(12)	O(10)#9-Na(2)-O(11)#2	95.32(12)
O(8)-Cd(2)-O(7)	54.40(11)	O(11)#2-Na(2)-O(11)#3	113.70(19)

[a] symmetry codes: #1 x+1, y, z; #2 -x+1/2, y+3/2, -z+3/2; #3 +3; #4 4; #5 -x-1/2, y+3/2, -z+1/2; #6 +4; #7 x+1/2, y+3/2, z+1; #8 x+1/2, y+3/2, z; #9 x, y, z.

Table S3 The selected bond lengths [Å] and angles [°] of compound **2**[a].

Cd(1)-O(7)#1	2.314(5)	K(1)-O(5)	2.778(5)
Cd(1)-O(5)	2.213(4)	K(1)-O(3)#2	2.672(4)
Cd(1)-O(2)	2.239(4)	K(1)-O(3)#5	2.672(4)
Cd(1)-O(3)#2	2.409(4)	K(1)-O(1)#4	2.707(5)
Cd(1)-O(4)#2	2.340(4)	K(1)-O(1)	2.707(5)
Cd(1)-O(8)#1	2.472(5)	Na(1)-O(6)	2.544(6)
Cd(1)-C(16)#1	2.724(7)	Na(1)-O(2)	2.419(6)
Cd(1)-C(8)#2	2.712(6)	Na(1)-O(8)#1	2.383(6)
Cd(2)-O(10)#3	2.325(4)	Na(1)-O(10)#3	2.400(5)
Cd(2)-O(10)	2.325(4)	Na(1)-O(11)	2.258(7)
Cd(2)-O(12)#3	2.336(6)	O(7)-Cd(1)#6	2.314(5)
Cd(2)-O(12)	2.336(6)	O(3)-Cd(1)#7	2.409(4)
Cd(2)-O(9)#3	2.475(5)	O(3)-K(1)#5	2.672(4)
Cd(2)-O(9)	2.475(5)	O(4)-Cd(1)#7	2.340(4)
Cd(2)-O(11)	2.581(5)	O(8)-Cd(1)#6	2.472(5)
Cd(2)-O(11)#3	2.581(5)	O(8)-Na(1)#6	2.383(6)
K(1)-O(5)#4	2.778(5)	O(10)-Na(1)#3	2.400(5)
O(7)#1-Cd(1)-O(3)#2	97.70(18)	O(12)#3-Cd(2)-O(11)	87.5(2)
O(7)#1-Cd(1)-O(4)#2	92.5(2)	O(12)-Cd(2)-O(11)	52.2(2)
O(7)#1-Cd(1)-O(8)#1	54.54(16)	O(12)#3-Cd(2)-O(11)#3	52.2(2)
O(5)-Cd(1)-O(7)#1	96.98(18)	O(9)-Cd(2)-O(9)#3	86.6(3)
O(5)-Cd(1)-O(2)	95.77(17)	O(9)#3-Cd(2)-O(11)	129.42(18)
O(5)-Cd(1)-O(3)#2	90.11(16)	O(9)#3-Cd(2)-O(11)#3	92.9(2)
O(5)-Cd(1)-O(4)#2	144.93(17)	O(9)-Cd(2)-O(11)#3	129.42(18)
O(5)-Cd(1)-O(8)#1	116.32(17)	O(9)-Cd(2)-O(11)	92.9(2)
O(2)-Cd(1)-O(7)#1	138.38(18)	O(11)-Cd(2)-O(11)#3	123.8(3)
O(2)-Cd(1)-O(3)#2	121.73(17)	O(5)#4-K(1)-O(5)	86.28(19)
O(2)-Cd(1)-O(4)#2	99.26(18)	O(3)#5-K(1)-O(5)	105.18(15)
O(2)-Cd(1)-O(8)#1	84.37(16)	O(3)#2-K(1)-O(5)	73.83(13)
O(3)#2-Cd(1)-O(8)#1	141.90(16)	O(3)#5-K(1)-O(5)#4	73.83(13)
O(4)#2-Cd(1)-O(3)#2	55.09(15)	O(3)#2-K(1)-O(5)#4	105.18(15)
O(4)#2-Cd(1)-O(8)#1	96.63(17)	O(3)#5-K(1)-O(3)#2	178.7(2)
O(10)#3-Cd(2)-O(10)	135.4(2)	O(3)#2-K(1)-O(1)#4	102.98(15)
O(10)#3-Cd(2)-O(12)	127.7(2)	O(3)#2-K(1)-O(1)	77.62(15)
O(10)-Cd(2)-O(12)#3	127.7(2)	O(3)#5-K(1)-O(1)	102.98(15)
O(10)#3-Cd(2)-O(12)#3	85.2(2)	O(3)#5-K(1)-O(1)#4	77.62(15)
O(10)-Cd(2)-O(12)	85.2(2)	O(1)#4-K(1)-O(5)	158.69(17)
O(10)#3-Cd(2)-O(9)#3	54.03(16)	O(1)-K(1)-O(5)	74.09(15)
O(10)-Cd(2)-O(9)	54.03(16)	O(1)-K(1)-O(5)#4	158.69(17)
O(10)#3-Cd(2)-O(9)	92.00(17)	O(1)#4-K(1)-O(5)#4	74.09(15)
O(10)-Cd(2)-O(9)#3	92.00(17)	O(1)#4-K(1)-O(1)	126.4(3)
O(10)#3-Cd(2)-O(11)#3	127.45(18)	O(2)-Na(1)-O(6)	80.25(19)
O(10)#3-Cd(2)-O(11)	75.48(17)	O(8)#1-Na(1)-O(6)	82.8(2)
O(10)-Cd(2)-O(11)	127.45(18)	O(8)#1-Na(1)-O(2)	82.56(17)
O(10)-Cd(2)-O(11)#3	75.48(17)	O(8)#1-Na(1)-O(10)#3	98.07(19)
O(12)-Cd(2)-O(12)#3	91.7(3)	O(10)#3-Na(1)-O(6)	170.4(2)
O(12)-Cd(2)-O(9)	90.8(2)	O(10)#3-Na(1)-O(2)	90.38(18)
O(12)#3-Cd(2)-O(9)#3	90.8(2)	O(11)-Na(1)-O(6)	103.9(2)
O(12)-Cd(2)-O(9)#3	177.0(2)	O(11)-Na(1)-O(2)	129.6(2)
O(12)#3-Cd(2)-O(9)	177.0(2)	O(11)-Na(1)-O(8)#1	147.7(3)

[a] symmetry codes: #1 x+1/2, y+3/2, z+1; #2 -x+1/2, y+3/2, -z+3/2; #3 x, y, z; #4 x+1, y, z; #5 4; #6 x+1/2, y+3/2, z; #7 -x-1/2, y+3/2, -z+1/2; #4 x+1, y, z; #5 4; #6 x+1/2, y+3/2, z; #7 -x-1/2, y+3/2, -z+1/2; #8 +3; #9 3.

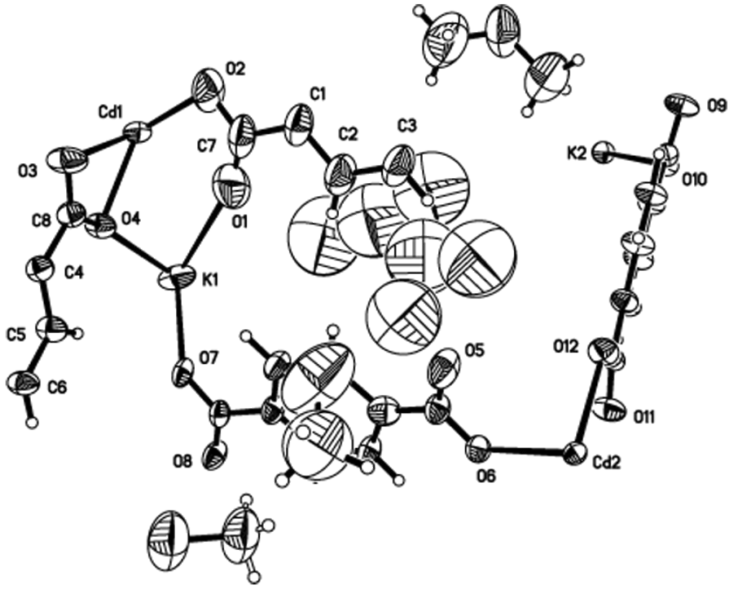

Fig. S12 ORTEP plot of the asymmetric unit of compound **3**, showing the labelling scheme and the 50% probability displacement ellipsoid.

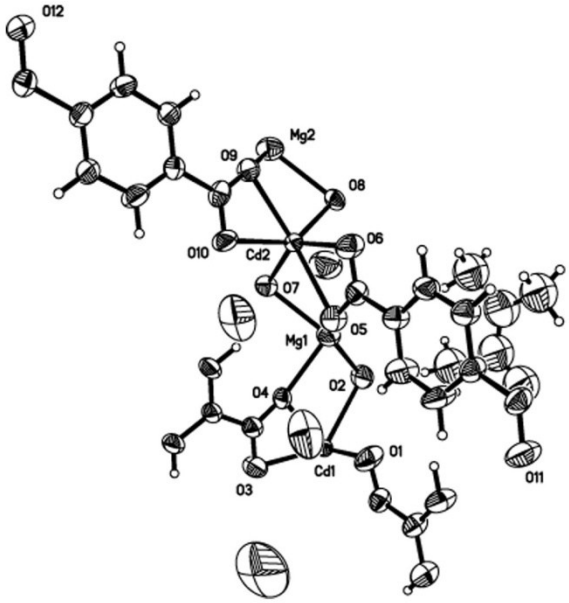

Fig. S13 ORTEP plot of the asymmetric unit of compound **4**, showing the labelling scheme and the 50% probability displacement ellipsoid.

Table S4 The selected bond lengths [Å] and angles [°] of compound **3**[a].

Cd(2)-O(6)	2.260(4)	K(2)-O(10)	2.676(4)
Cd(2)-O(12)	2.240(4)	K(2)-O(11)#5	2.731(5)
Cd(2)-O(7)#2	2.377(4)	K(2)-O(11)#1	2.731(5)
Cd(2)-O(8)#2	2.364(4)	K(1)-Cd(2)#6	3.6251(19)
Cd(2)-O(10)#3	2.434(4)	K(1)-O(12)#6	2.763(5)
Cd(2)-O(9)#3	2.309(4)	K(1)-O(7)	2.563(5)
Cd(2)-C(15)#2	2.703(6)	K(1)-O(4)	2.584(5)
Cd(2)-C(24)#3	2.714(6)	K(1)-O(5)#6	2.742(5)
Cd(1)-O(4)	2.299(4)	K(1)-O(2)#4	2.614(7)
Cd(1)-O(4)#4	2.299(4)	K(1)-O(1)	3.353(9)
Cd(1)-O(3)#4	2.487(5)	O(6)-K(2)#1	2.822(5)
Cd(1)-O(3)	2.487(5)	O(12)-K(1)#2	2.763(5)
Cd(1)-O(2)	2.281(7)	O(7)-Cd(2)#6	2.378(4)
Cd(1)-O(2)#4	2.281(7)	O(8)-Cd(2)#6	2.364(4)
K(2)-O(6)#1	2.822(5)	O(10)-Cd(2)#5	2.434(4)
K(2)-O(6)#5	2.822(5)	O(11)-K(2)#1	2.731(5)
K(2)-O(10)#4	2.676(4)	O(9)-Cd(2)#5	2.309(4)
O(6)-Cd(2)-O(7)#2	119.82(16)	O(2)#4-Cd(1)-O(2)	116.5(4)
O(6)-Cd(2)-O(8)#2	97.37(17)	O(6)#1-K(2)-O(6)#5	85.27(18)
O(6)-Cd(2)-O(10)#3	89.44(15)	O(10)#4-K(2)-O(6)#5	102.20(13)
O(6)-Cd(2)-O(9)#3	144.07(16)	O(10)#4-K(2)-O(6)#1	73.84(12)
O(12)-Cd(2)-O(6)	92.59(16)	O(10)-K(2)-O(6)#1	102.20(13)
O(12)-Cd(2)-O(7)#2	84.87(16)	O(10)-K(2)-O(10)#4	174.8(2)
O(12)-Cd(2)-O(8)#2	138.65(17)	O(10)-K(2)-O(11)#1	101.94(14)
O(12)-Cd(2)-O(10)#3	127.21(16)	O(10)-K(2)-O(11)#5	80.15(14)
O(12)-Cd(2)-O(9)#3	103.96(17)	O(10)#4-K(2)-O(11)#1	80.15(14)
O(7)#2-Cd(2)-O(10)#3	137.23(15)	O(10)#4-K(2)-O(11)#5	101.94(14)
O(8)#2-Cd(2)-O(7)#2	55.46(15)	O(11)#1-K(2)-O(6)#1	71.07(14)
O(8)#2-Cd(2)-O(10)#3	93.04(16)	O(11)#5-K(2)-O(6)#5	71.07(14)
O(9)#3-Cd(2)-O(7)#2	93.60(17)	O(11)#1-K(2)-O(6)#5	154.71(15)
O(9)#3-Cd(2)-O(8)#2	90.94(19)	O(11)#5-K(2)-O(6)#1	154.71(15)
O(9)#3-Cd(2)-O(10)#3	55.14(14)	O(11)#5-K(2)-O(11)#1	133.6(2)
O(4)-Cd(1)-O(4)#4	137.2(3)	O(12)#6-K(1)-O(1)	139.5(2)
O(4)#4-Cd(1)-O(3)	93.55(18)	O(7)-K(1)-O(12)#6	71.53(14)
O(4)-Cd(1)-O(3)	54.20(16)	O(7)-K(1)-O(4)	95.74(15)
O(4)#4-Cd(1)-O(3)#4	54.20(16)	O(7)-K(1)-O(5)#6	77.76(17)
O(4)-Cd(1)-O(3)#4	93.55(18)	O(7)-K(1)-O(2)#4	163.4(2)
O(3)#4-Cd(1)-O(3)	88.4(3)	O(7)-K(1)-O(1)	96.9(2)
O(2)-Cd(1)-O(4)#4	83.8(2)	O(4)-K(1)-O(12)#6	80.24(16)
O(2)-Cd(1)-O(4)	119.4(2)	O(4)-K(1)-O(5)#6	154.54(19)
O(2)#4-Cd(1)-O(4)	83.8(2)	O(4)-K(1)-O(2)#4	72.12(17)
O(2)#4-Cd(1)-O(4)#4	119.4(2)	O(4)-K(1)-O(1)	62.0(2)
O(2)-Cd(1)-O(3)#4	137.8(2)	O(2)#4-K(1)-O(12)#6	116.0(2)
O(2)-Cd(1)-O(3)	90.8(2)	O(2)#4-K(1)-O(5)#6	118.1(2)
O(2)#4-Cd(1)-O(3)#4	90.8(2)	O(2)#4-K(1)-O(1)	67.6(2)

[a] symmetry codes: #1 -x+3/2, -y+3/2, -z+1; #2 x, -y+1, z+1/2; #3 x+1/2, -y+3/2, z+1/2; #4 -x+1, y, -z+1/2; #5 x-1/2, -y+3/2, z-1/2; #6 x, -y+1, z-1/2; #7 -x+3/2, -y+1/2, -z+1; #8 -x+1, -y+1, -z+1.

Table S5 The selected bond lengths [Å] and angles [°] of compound **4**[a].

Cd(1)-O(1)	2.315(5)	Cd(2)-C(9)	2.749(6)
Cd(1)-O(1)#1	2.315(5)	Cd(2)-C(17)	2.708(6)
Cd(1)-O(3)#1	2.454(5)	Mg(2)-O(9)	2.425(4)
Cd(1)-O(3)	2.454(5)	Mg(2)-O(9)#2	2.425(4)
Cd(1)-O(4)#1	2.342(4)	Mg(2)-O(12)#3	2.541(5)
Cd(1)-O(4)	2.342(4)	Mg(2)-O(12)#4	2.541(5)
Cd(1)-O(2)#1	2.549(5)	Mg(2)-O(8)	2.462(5)
Cd(1)-O(2)	2.549(5)	Mg(2)-O(8)#2	2.462(5)
Cd(2)-O(6)	2.283(5)	Mg(1)-O(7)	2.387(5)
Cd(2)-O(9)	2.418(4)	Mg(1)-O(11)#5	2.461(5)
Cd(2)-O(7)	2.223(4)	Mg(1)-O(5)	2.374(5)
Cd(2)-O(8)	2.230(4)	Mg(1)-O(4)	2.347(5)
Cd(2)-O(5)	2.526(5)	Mg(1)-O(2)	2.256(5)
Cd(2)-O(10)	2.315(4)	O(11)-Mg(1)#6	2.461(5)
O(1)-Cd(1)-O(1)#1	90.9(3)	O(7)-Cd(2)-O(5)	85.86(15)
O(1)#1-Cd(1)-O(3)	175.70(19)	O(7)-Cd(2)-O(10)	98.40(18)
O(1)-Cd(1)-O(3)#1	175.70(18)	O(8)-Cd(2)-O(6)	97.55(18)
O(1)-Cd(1)-O(3)	92.5(2)	O(8)-Cd(2)-O(9)	87.80(15)
O(1)#1-Cd(1)-O(3)#1	92.5(2)	O(8)-Cd(2)-O(5)	116.54(17)
O(1)-Cd(1)-O(4)#1	128.52(16)	O(8)-Cd(2)-O(10)	142.58(16)
O(1)-Cd(1)-O(4)	85.84(18)	O(10)-Cd(2)-O(9)	55.02(14)
O(1)#1-Cd(1)-O(4)	128.52(16)	O(10)-Cd(2)-O(5)	99.12(17)
O(1)#1-Cd(1)-O(4)#1	85.84(18)	O(9)#2-Mg(2)-O(9)	174.2(3)
O(1)#1-Cd(1)-O(2)#1	86.1(2)	O(9)-Mg(2)-O(12)#4	81.59(16)
O(1)-Cd(1)-O(2)	86.1(2)	O(9)#2-Mg(2)-O(12)#4	95.23(16)
O(1)#1-Cd(1)-O(2)	52.96(16)	O(9)-Mg(2)-O(12)#3	95.23(16)
O(1)-Cd(1)-O(2)#1	52.96(16)	O(9)#2-Mg(2)-O(12)#3	81.59(16)
O(3)#1-Cd(1)-O(3)	84.3(3)	O(9)-Mg(2)-O(8)	82.60(15)
O(3)-Cd(1)-O(2)#1	93.72(19)	O(9)#2-Mg(2)-O(8)	101.69(16)
O(3)#1-Cd(1)-O(2)#1	129.98(15)	O(9)-Mg(2)-O(8)#2	101.69(16)
O(3)#1-Cd(1)-O(2)	93.72(19)	O(9)#2-Mg(2)-O(8)#2	82.60(15)
O(3)-Cd(1)-O(2)	129.98(15)	O(12)#4-Mg(2)-O(12)#3	113.5(3)
O(4)#1-Cd(1)-O(3)	89.96(17)	O(8)#2-Mg(2)-O(12)#3	80.61(15)
O(4)-Cd(1)-O(3)#1	89.96(17)	O(8)-Mg(2)-O(12)#4	80.61(15)
O(4)#1-Cd(1)-O(3)#1	54.50(15)	O(8)-Mg(2)-O(12)#3	165.3(2)
O(4)-Cd(1)-O(3)	54.50(15)	O(8)#2-Mg(2)-O(12)#4	165.3(2)
O(4)#1-Cd(1)-O(4)	133.8(2)	O(8)-Mg(2)-O(8)#2	85.6(2)
O(4)-Cd(1)-O(2)#1	128.56(16)	O(7)-Mg(1)-O(11)#5	80.61(18)
O(4)#1-Cd(1)-O(2)#1	75.57(15)	O(5)-Mg(1)-O(7)	85.85(17)
O(4)#1-Cd(1)-O(2)	128.56(16)	O(5)-Mg(1)-O(11)#5	84.0(2)
O(4)-Cd(1)-O(2)	75.57(15)	O(4)-Mg(1)-O(7)	92.15(18)
O(2)#1-Cd(1)-O(2)	123.0(3)	O(4)-Mg(1)-O(11)#5	172.5(2)
O(6)-Cd(2)-O(9)	101.32(17)	O(4)-Mg(1)-O(5)	97.43(19)
O(6)-Cd(2)-O(5)	54.16(16)	O(2)-Mg(1)-Cd(2)	161.93(17)
O(6)-Cd(2)-O(10)	94.2(2)	O(2)-Mg(1)-O(7)	136.9(2)
O(9)-Cd(2)-O(5)	145.62(15)	O(2)-Mg(1)-O(11)#5	102.6(2)
O(7)-Cd(2)-O(6)	139.56(17)	O(2)-Mg(1)-O(5)	137.1(2)
O(7)-Cd(2)-O(9)	117.39(16)	O(2)-Mg(1)-O(4)	81.35(18)

[a] symmetry codes: #1 x+2, y, z+1; #2 x+1, y, z+1; #3 4; #4 -x+1/2, y+3/2, -z+3/2; #5 x+1/2, y+3/2, z+1; #6 x+1/2, y+3/2, z; #7 +5; #8 -x-1/2, y+3/2, -z+1/2; #9 +5.

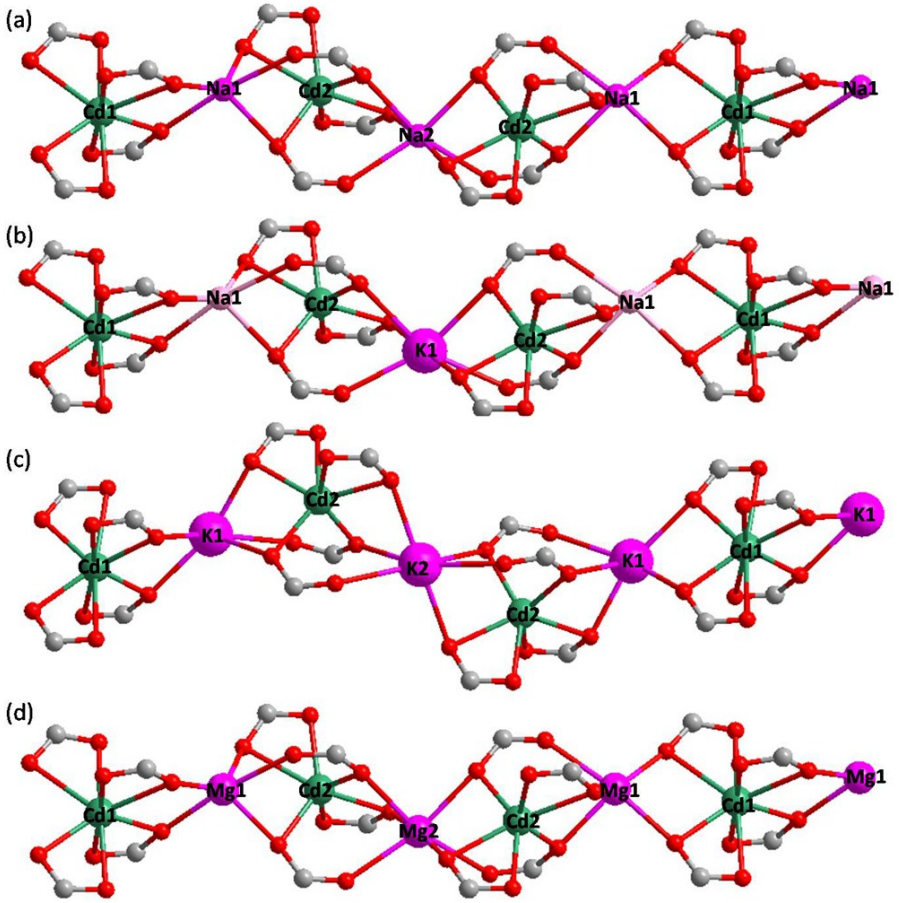

Fig. S14 (a)-(d) the {Cd-O-M} inorganic chain contained in **1**, **2**, **3**, and **4**, respectively.

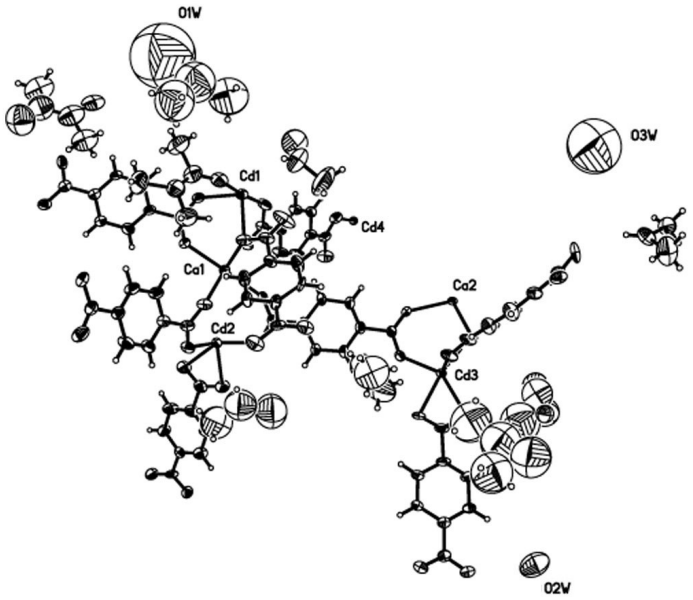

Fig. S15 ORTEP plot of the asymmetric unit of compound **5**, showing the labelling scheme and the 50% probability displacement ellipsoid.

Table S6 The selected bond lengths [Å] and angles [°] of compound **5**[a].

Cd(1)-O(22)	2.203(8)	Cd(4)-O(4)#4	2.285(8)
Cd(1)-O(26)	2.217(8)	Cd(4)-O(16)#5	2.329(9)
Cd(1)-O(8)#8	2.249(9)	Cd(4)-O(15)#5	2.365(8)
Cd(1)-O(29)	2.323(8)	O(1)-Ca(2)	2.379(7)
Cd(1)-O(33)	2.363(8)	O(4)-Cd(4)#9	2.285(8)
Cd(1)-O(7)#8	2.560(9)	O(4)-Ca(2)#10	2.356(8)
Cd(1)-C(15)#8	2.753(12)	O(7)-Cd(1)#1	2.560(9)
Cd(2)-O(18)	2.249(7)	O(8)-Cd(1)#1	2.249(9)
Cd(2)-O(31)#7	2.294(8)	O(10)-Ca(2)	2.296(8)
Cd(2)-O(13)	2.310(8)	O(12)-Ca(1)	2.254(8)
Cd(2)-O(14)	2.406(8)	O(15)-Cd(4)#2	2.365(8)
Cd(2)-O(32)#7	2.527(8)	O(16)-Cd(4)#2	2.329(9)
Cd(3)-O(2)	2.478(8)	O(17)-Ca(1)	2.288(8)
Cd(3)-O(9)	2.168(8)	O(19)-Cd(3)#11	2.224(8)
Cd(3)-O(19)#3	2.224(8)	O(20)-Ca(2)#11	2.275(8)
Cd(3)-O(1)	2.321(7)	O(21)-Ca(1)	2.280(8)
Cd(3)-O(5)	2.322(8)	O(24)-Ca(2)#6	2.271(9)
Cd(3)-O(6)	2.367(8)	O(25)-Ca(1)	2.291(8)
Cd(4)-O(28)#3	2.199(7)	O(27)-Ca(2)#7	2.237(8)
Cd(4)-O(23)	2.210(7)	O(28)-Cd(4)#11	2.199(7)
Ca(2)-O(27)#12	2.237(8)	O(29)-Ca(1)	2.322(8)
Ca(2)-O(24)#10	2.271(9)	O(31)-Cd(2)#12	2.294(8)
Ca(2)-O(20)#3	2.275(8)	O(31)-Ca(1)#12	2.385(8)
Ca(2)-O(4)#6	2.356(8)	O(32)-Cd(2)#12	2.527(8)
O(28)#3-Cd(4)-O(23)	107.2(3)	O(26)-Cd(1)-O(8)#8	133.3(3)
O(28)#3-Cd(4)-O(4)#4	107.8(3)	O(22)-Cd(1)-O(29)	96.6(3)
O(23)-Cd(4)-O(4)#4	103.7(3)	O(26)-Cd(1)-O(29)	96.0(3)
O(28)#3-Cd(4)-O(16)#5	81.1(3)	O(8)#8-Cd(1)-O(29)	128.8(3)
O(23)-Cd(4)-O(16)#5	113.3(4)	O(22)-Cd(1)-O(33)	174.4(3)
O(4)#4-Cd(4)-O(16)#5	137.5(3)	O(26)-Cd(1)-O(33)	85.7(3)
O(28)#3-Cd(4)-O(15)#5	136.1(3)	O(8)#8-Cd(1)-O(33)	86.2(3)
O(23)-Cd(4)-O(15)#5	96.1(3)	O(29)-Cd(1)-O(33)	85.0(3)
O(4)#4-Cd(4)-O(15)#5	101.8(3)	O(22)-Cd(1)-O(7)#8	90.9(3)
O(16)#5-Cd(4)-O(15)#5	55.4(3)	O(26)-Cd(1)-O(7)#8	79.5(3)
O(9)-Cd(3)-O(19)#3	104.4(4)	O(8)#8-Cd(1)-O(7)#8	54.4(3)
O(9)-Cd(3)-O(1)	109.6(3)	O(29)-Cd(1)-O(7)#8	171.9(3)
O(19)#3-Cd(3)-O(1)	97.3(3)	O(33)-Cd(1)-O(7)#8	87.9(3)
O(9)-Cd(3)-O(5)	87.1(3)	O(27)#12-Ca(2)-O(24)#10	89.8(4)
O(19)#3-Cd(3)-O(5)	105.2(3)	O(27)#12-Ca(2)-O(20)#3	168.1(3)
O(1)-Cd(3)-O(5)	147.8(3)	O(24)#10-Ca(2)-O(20)#3	95.1(3)
O(9)-Cd(3)-O(6)	143.1(3)	O(27)#12-Ca(2)-O(10)	87.8(3)
O(19)#3-Cd(3)-O(6)	88.7(3)	O(24)#10-Ca(2)-O(10)	167.7(3)
O(1)-Cd(3)-O(6)	102.6(3)	O(20)#3-Ca(2)-O(10)	89.7(3)
O(5)-Cd(3)-O(6)	56.1(3)	O(27)#12-Ca(2)-O(4)#6	89.4(3)
O(9)-Cd(3)-O(2)	99.1(4)	O(24)#10-Ca(2)-O(4)#6	78.4(3)

O(19)#3-Cd(3)-O(2)	148.5(3)	O(20)#3-Ca(2)-O(4)#6	102.2(3)
O(1)-Cd(3)-O(2)	54.7(3)	O(10)-Ca(2)-O(4)#6	89.5(3)
O(5)-Cd(3)-O(2)	96.6(3)	O(27)#12-Ca(2)-O(1)	88.2(3)
O(6)-Cd(3)-O(2)	84.9(3)	O(24)#10-Ca(2)-O(1)	94.2(3)
O(9)-Cd(3)-C(16)	114.2(4)	O(20)#3-Ca(2)-O(1)	80.7(3)
O(11)-Cd(2)-O(18)	107.5(3)	O(10)-Ca(2)-O(1)	97.8(3)
O(11)-Cd(2)-O(31)#7	110.4(3)	O(4)#6-Ca(2)-O(1)	172.2(3)
O(18)-Cd(2)-O(31)#7	98.0(3)	O(12)-Ca(1)-O(21)	86.1(4)
O(11)-Cd(2)-O(13)	89.4(3)	O(12)-Ca(1)-O(17)	87.1(3)
O(18)-Cd(2)-O(13)	103.9(3)	O(21)-Ca(1)-O(17)	169.4(3)
O(31)#7-Cd(2)-O(13)	144.4(3)	O(12)-Ca(1)-O(25)	177.1(4)
O(11)-Cd(2)-O(14)	144.6(3)	O(21)-Ca(1)-O(25)	96.7(3)
O(18)-Cd(2)-O(14)	88.7(3)	O(17)-Ca(1)-O(25)	90.3(3)
O(31)#7-Cd(2)-O(14)	97.7(3)	O(12)-Ca(1)-O(29)	93.5(3)
O(13)-Cd(2)-O(14)	55.7(3)	O(21)-Ca(1)-O(29)	88.3(3)
O(11)-Cd(2)-O(32)#7	99.0(3)	O(17)-Ca(1)-O(29)	100.2(3)
O(18)-Cd(2)-O(32)#7	146.8(3)	O(25)-Ca(1)-O(29)	85.6(3)
O(31)#7-Cd(2)-O(32)#7	53.1(3)	O(12)-Ca(1)-O(31)#7	87.2(3)
O(13)-Cd(2)-O(32)#7	95.8(3)	O(21)-Ca(1)-O(31)#7	95.6(3)
O(14)-Cd(2)-O(32)#7	80.6(3)	O(17)-Ca(1)-O(31)#7	76.0(3)
O(22)-Cd(1)-O(26)	99.5(3)	O(25)-Ca(1)-O(31)#7	93.5(3)
O(22)-Cd(1)-O(8)#8	88.6(3)	O(29)-Ca(1)-O(31)#7	176.1(3)

[a] symmetry codes: #1 -x+2, -y+1, z-1/2; #2 -x+1, -y+1, z-1/2; #3 x, y+1, z; #4 x-1, y, z; #5 -x+1, -y+1, z+1/2; #6 x-1/2, -y+3/2, z; #7 x-1/2, -y+1/2, z; #8 -x+2, -y+1, z+1/2; #9 x+1, y, z; #10 x+1/2, -y+3/2, z; #11 x, y-1, z; #12 x+1/2, -y+1/2, z.

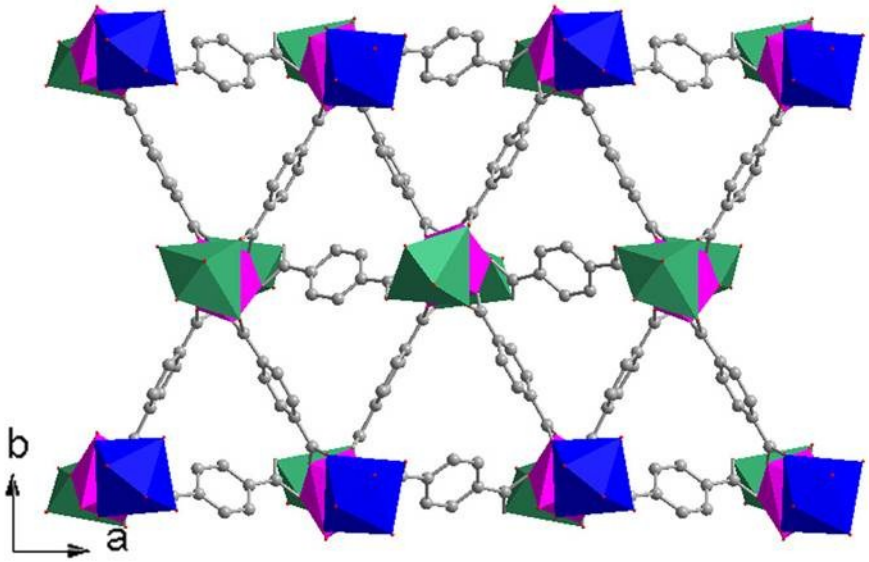

Fig. S16 The layer structure contained in **5**.

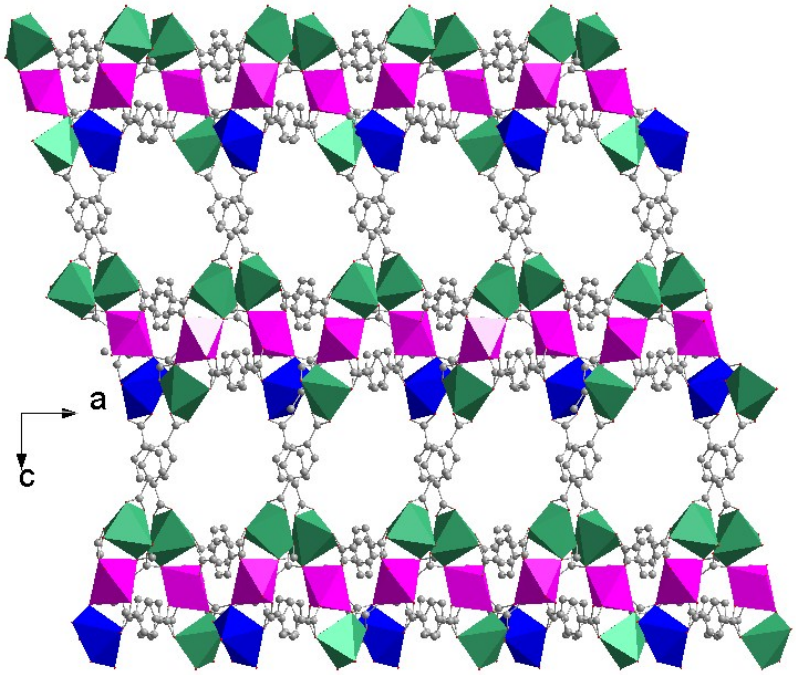

Fig. S17 Polyhedron view of **5** along [010] direction.

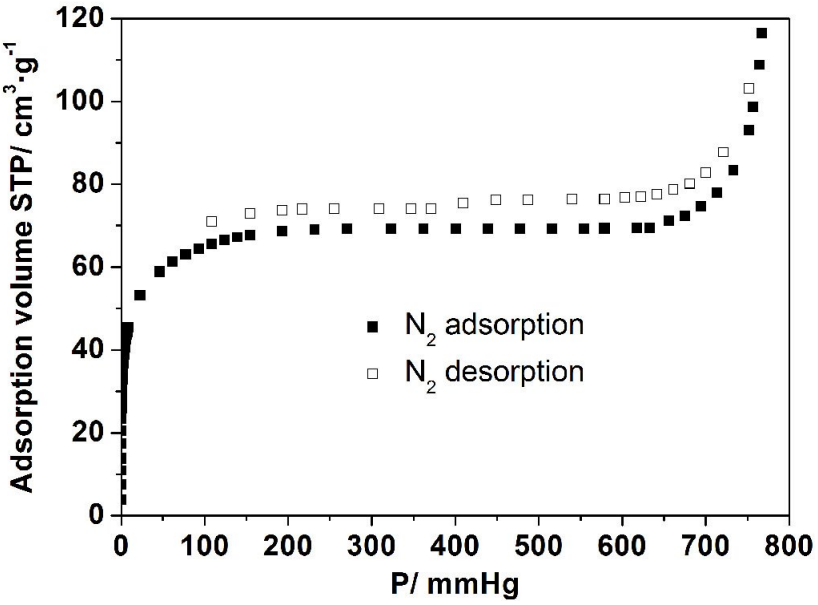

Fig. S18 N_2 adsorption/desorption isotherms of 5 at 77 K.

5. Solid-state fluorescent properties of H_2BDC

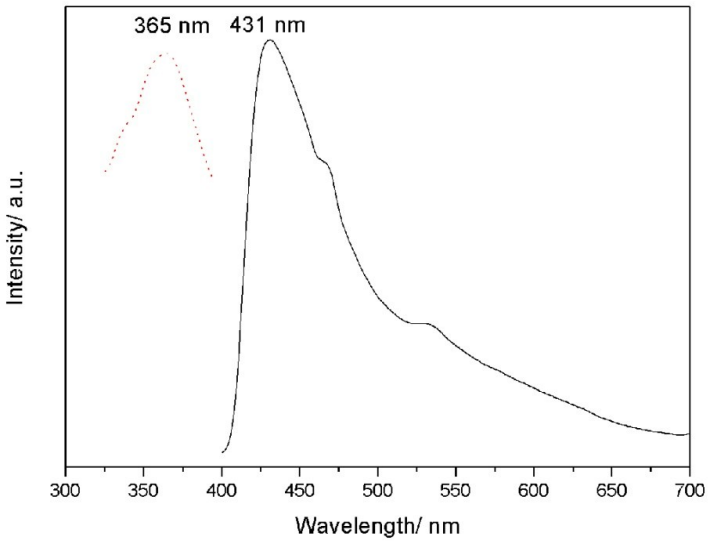

Fig. S19 The solid state fluorescent properties of H_2BDC at room temperature.

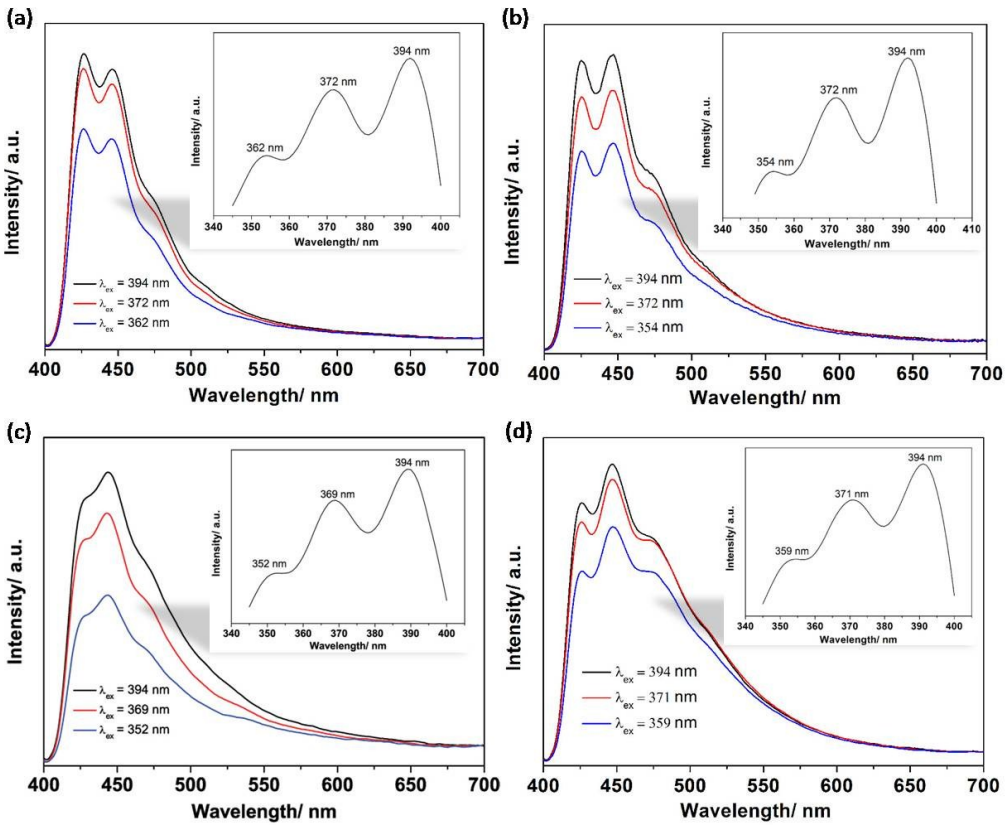

Fig. S20 (a)-(d) the solid state fluorescent properties of **1**, **2**, **3**, and **5,** respectively, at room temperature.

6. Stern-Volmer plots for high explosives added to the emulsion of **5** with linear and non-linear fitting curves.

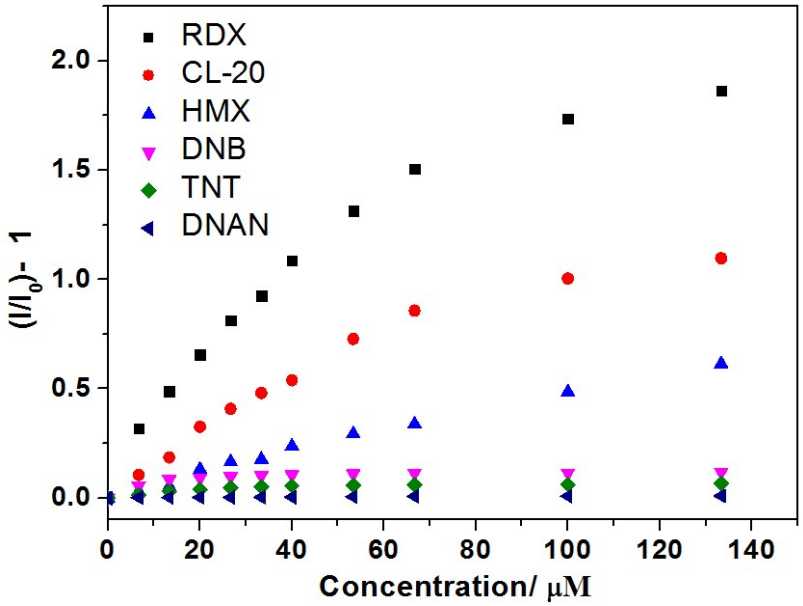

Fig. S21 Stern-Volmer plots for high explosives analytes added to the emulsion of **5**.

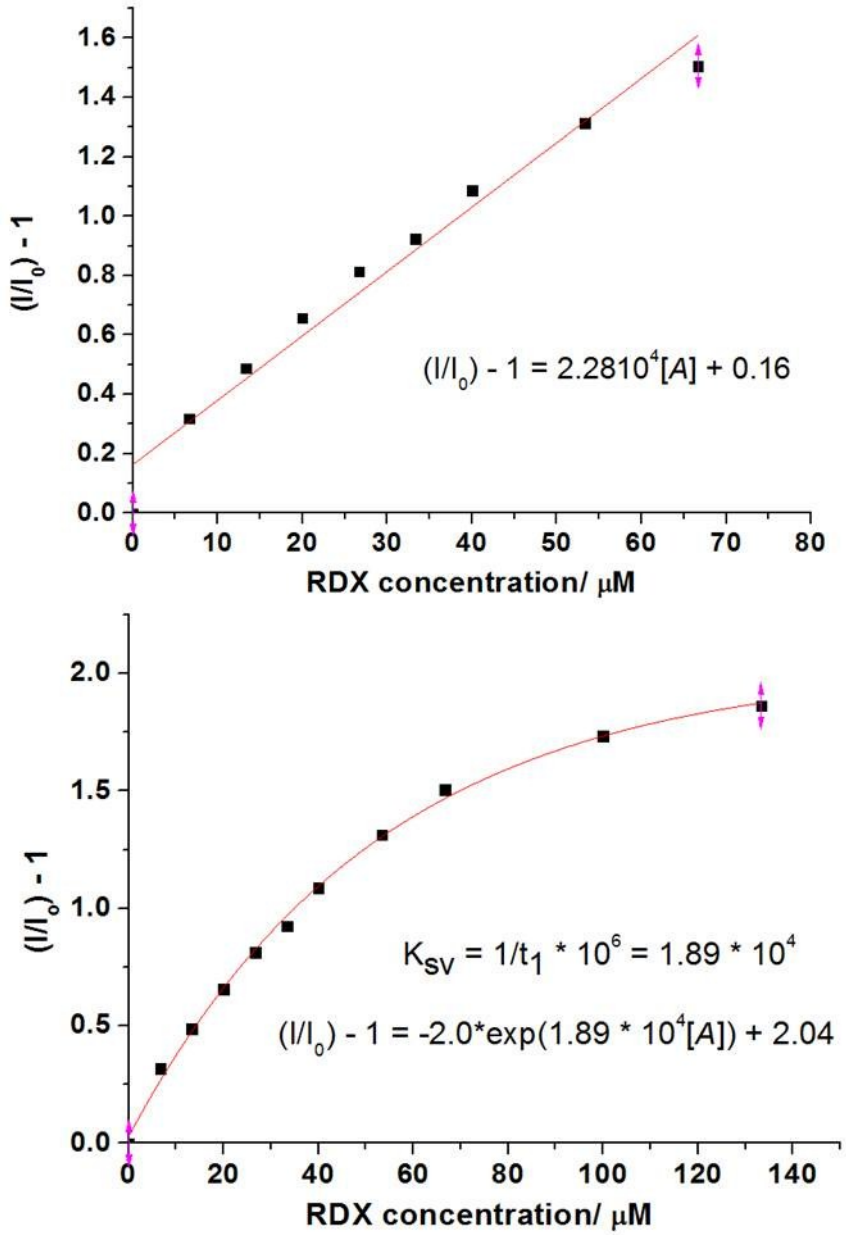

Fig. S22 Stern-Volmer plots for RDX added to the emulsion of **5** with linear and non-linear fitting curves.

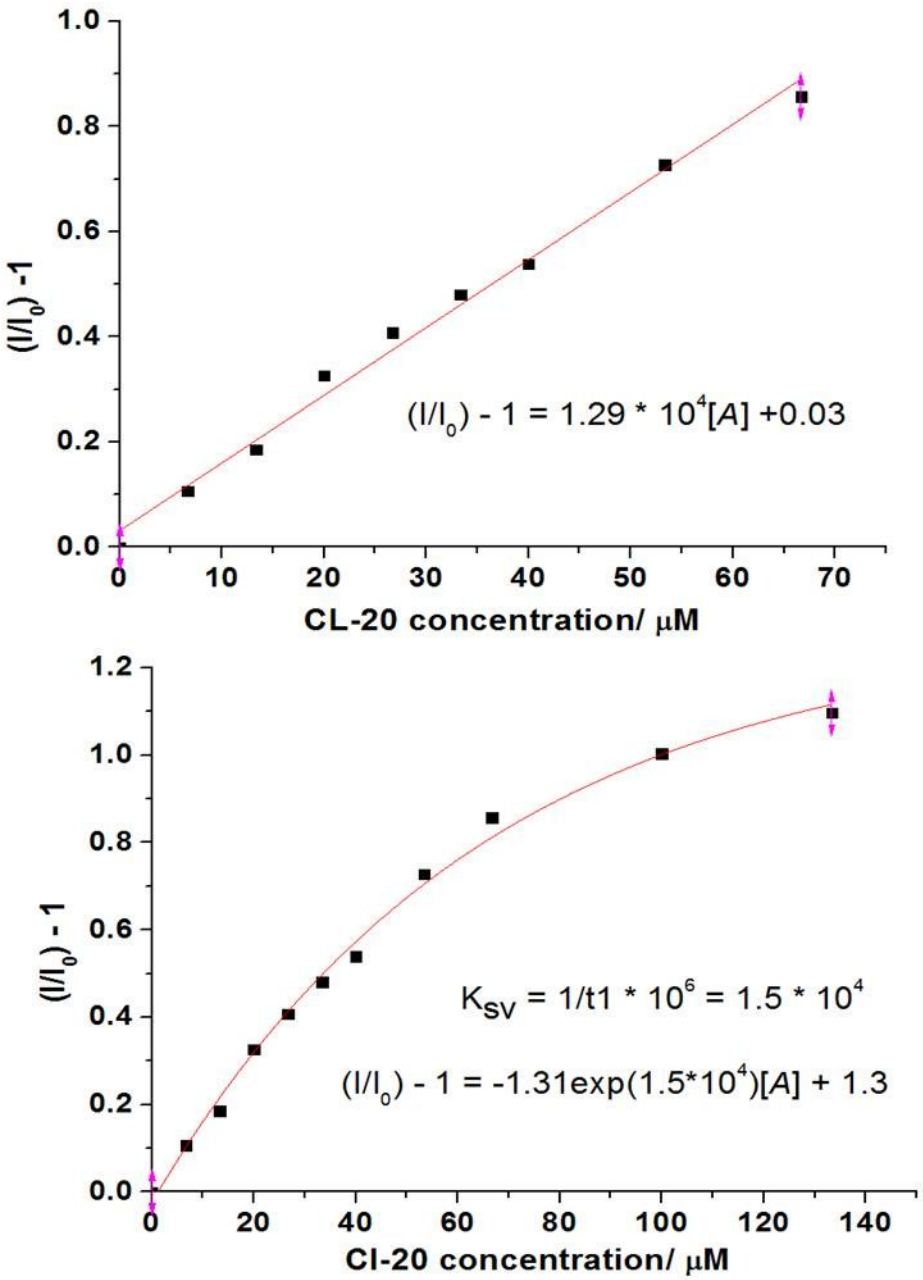

Fig. S23 Stern-Volmer plots for CL-20 added to the emulsion of **5** with linear and non-linear fitting curves.

7. HOMO and LUMO energies for explosive analytes and 5

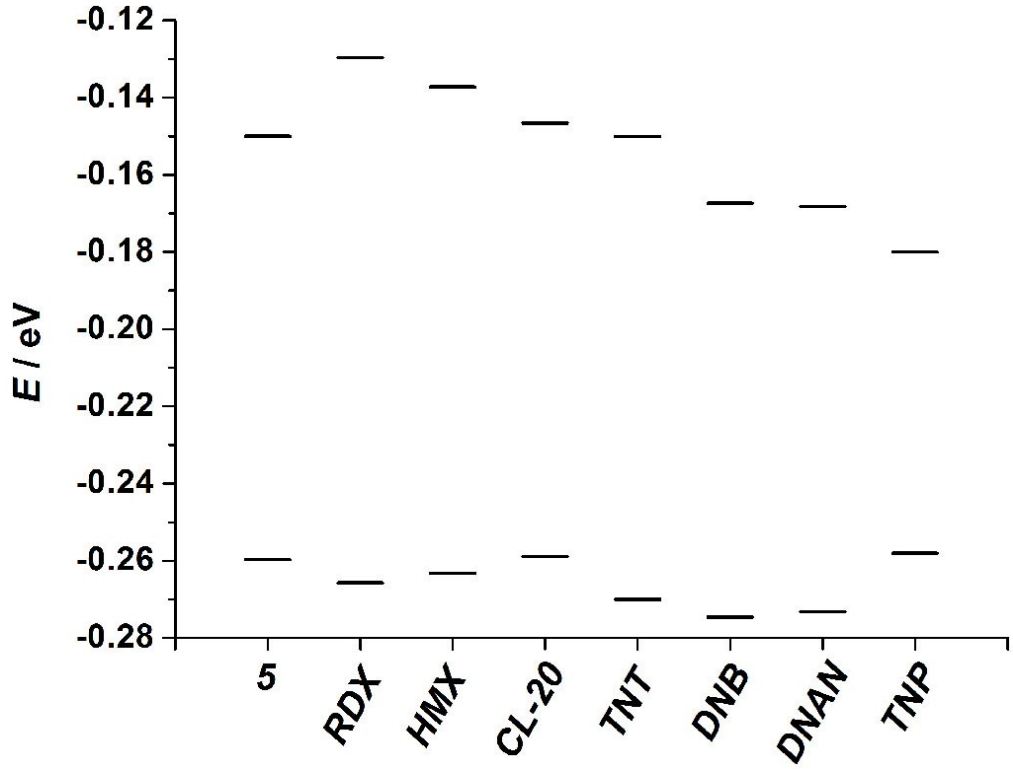

Fig. S24 HOMO and LUMO energies for explosive analytes and **5**.

8. The emission spectra of 5 dispersed in acetonitrile upon increment addition of different explosive analytes

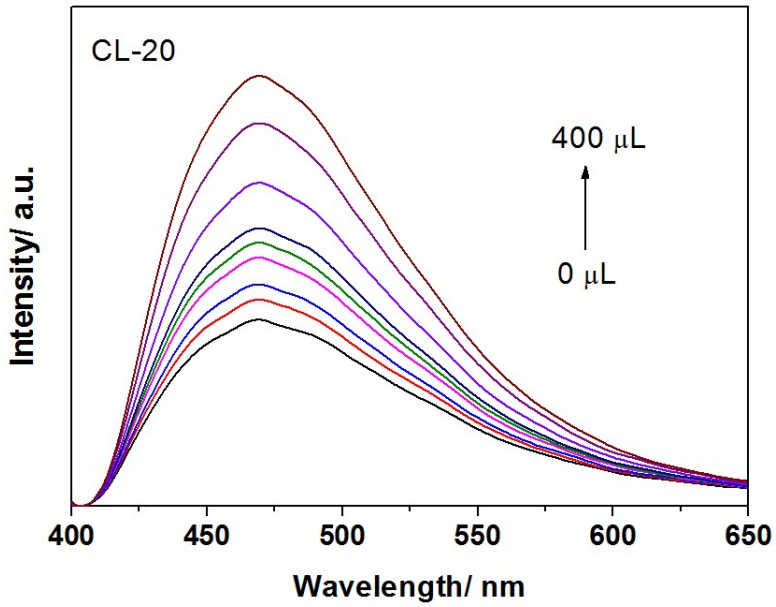

Fig. S25 The emission spectra of **5** dispersed in acetonitrile upon increment addition of a CL-20 acetonitrile solution (1 mM), upon excited λ_{ex} = 361 nm.

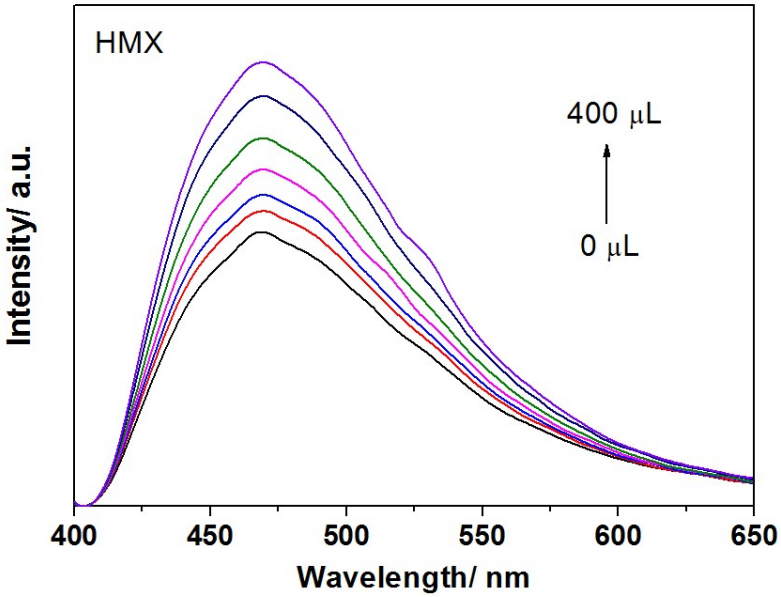

Fig. S26 The emission spectra of **5** dispersed in acetonitrile upon increment addition of a HMX acetonitrile solution (1 mM), upon excited λ_{ex} = 361 nm.

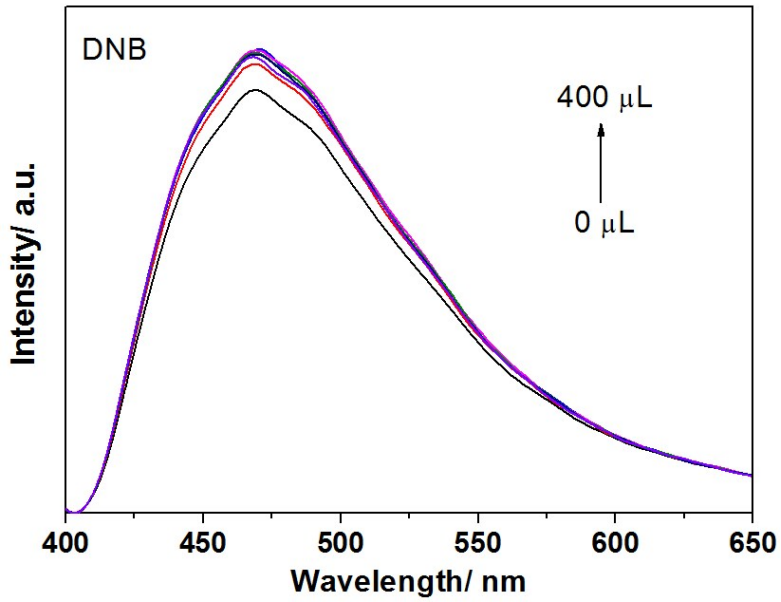

Fig. S27 The emission spectra of **5** dispersed in acetonitrile upon increment addition of a DNB acetonitrile solution (1 mM), upon excited λ_{ex} = 361 nm.

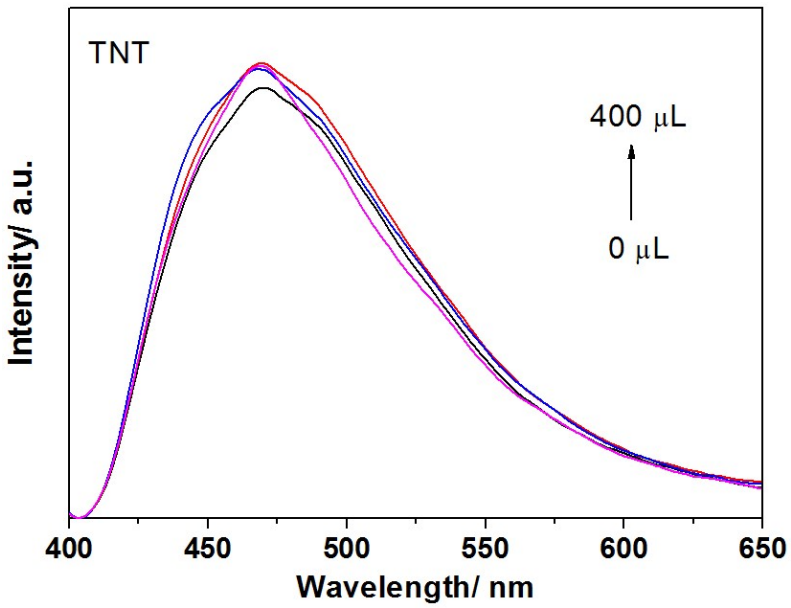

Fig. S28 The emission spectra of **5** dispersed in acetonitrile upon increment addition of a TNT acetonitrile solution (1 mM), upon excited λ_{ex} = 361 nm.

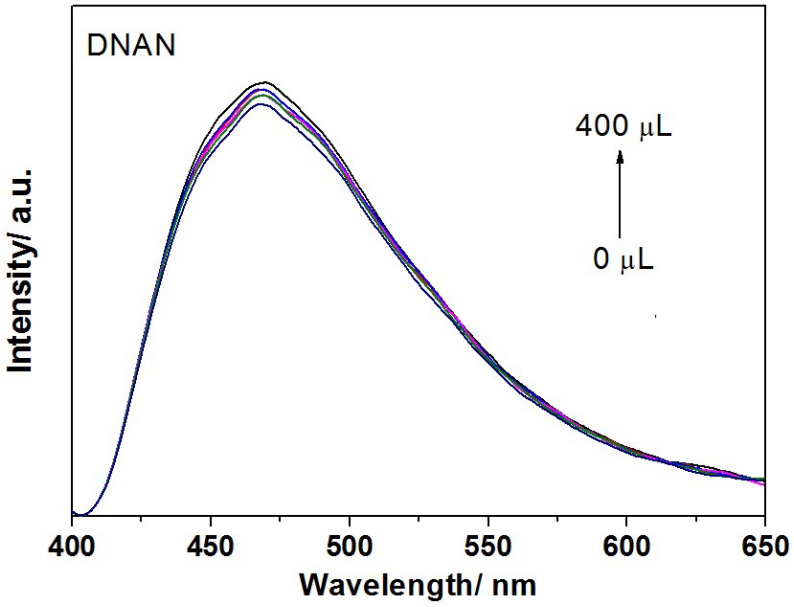

Fig. S29 The emission spectra of **5** dispersed in acetonitrile upon increment addition of a DNAN acetonitrile solution (1 mM), upon excited λ_{ex} = 361 nm.

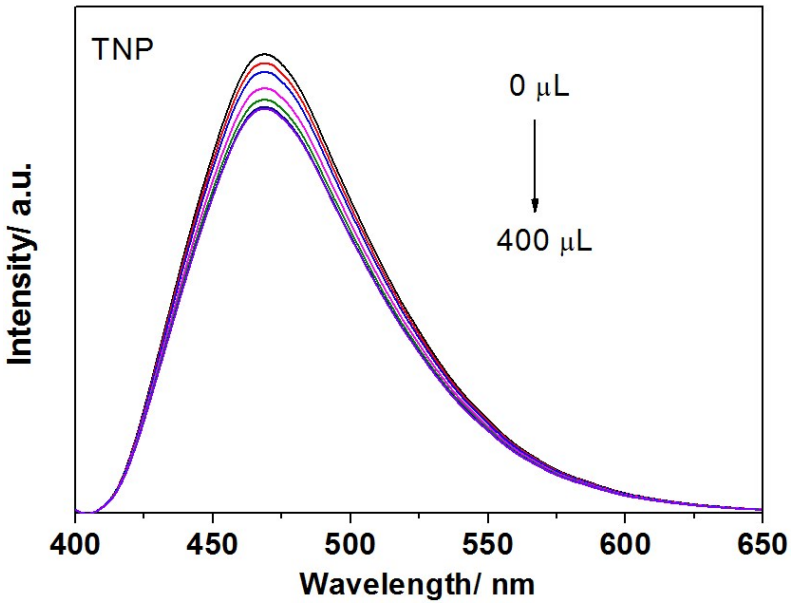

Fig. S30 The emission spectra of **5** dispersed in acetonitrile upon increment addition of a TNP acetonitrile solution (1 mM), upon excited λ_{ex} = 361 nm.

9. the recyclability of compound 5 for sensing nitro explosive RDX

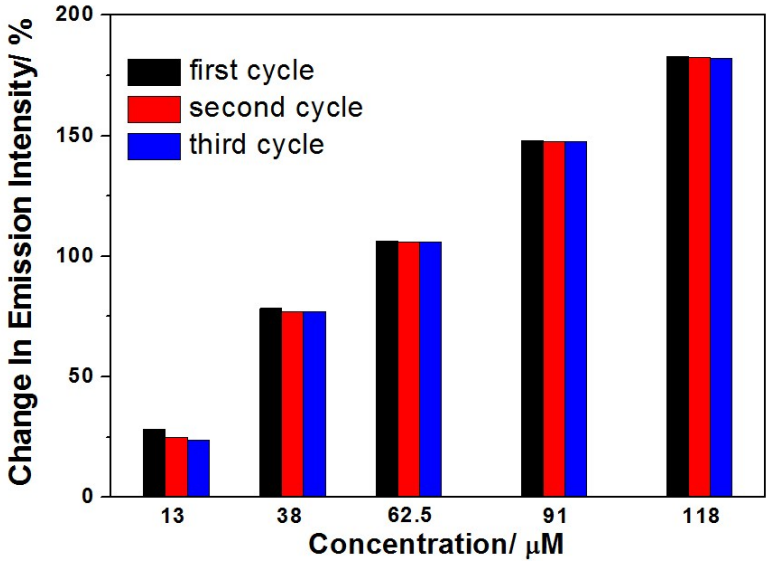

Fig. 31 The recyclability of compound **5** for sensing nitro explosive RDX.

10. XRD curves of **5** under different conditions

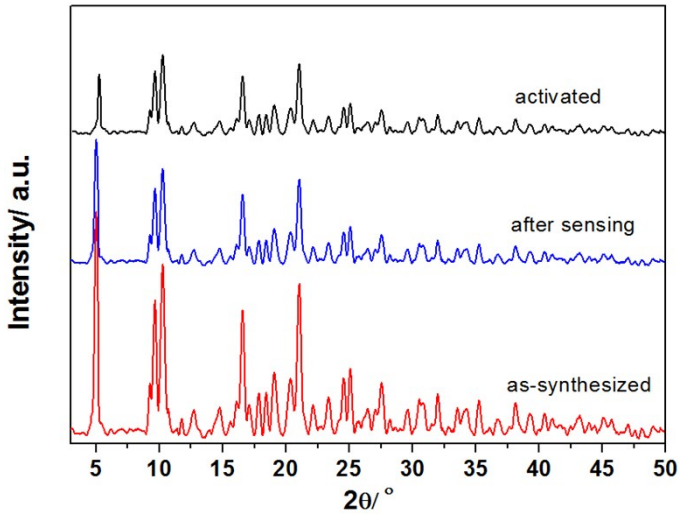

Fig. 32 The powder XRD patterns of as-synthesized, after sensing experimental towards RDX, and degassed sample of compound **5**.