Supporting Information for

Alkaline-Earth Metal Based MOFs with Second Scale Long-Lasting Phosphor Behavior

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S1. SEM micrographs



Figure S1. SEM micrographs on crystals of compound 1.



Figure S2. SEM micrographs on crystals of compound 2.



Figure S3. SEM micrographs of compound 3.

S2. Details on crystal structures of 1–3



Figure S4. Asymmetric units corresponding to compounds **1-3**. Color code: N = blue, C = grey, O = red, Ca = green, Ba = cyan. Hydrogen atoms have been omitted for clarity.



Scheme S1. Coordination modes shown by four crystallographically independent btb ligands in compound 1.



Scheme S2. Coordination modes shown by two crystallographically independent bdc ligands in compound 2 and NH_2 -bdc ligand in compound 3.



Scheme S3. Coordination polyhedra of compounds 1–3.



Figure S5. Void channel system of compound 1 along: (a) c axis and (b) arbitrary axis.



Figure S6. Packing of compound 2 showing solvent accessible voids.

S3. Selected bonds and angles

Table S1. Selected	ed distances ((Å) for comp	ounds 1-3.

	1	2	3
$C_{21} O5A 2 328(4)$	$\frac{1}{C2T N1T 1 57(2)}$	$\frac{2}{C_{21}}$	Bal OIC 2 652(8)
$C_{a1} OIV 2 320(4)$	$C_{211}N_{111} 1.37(2)$	$C_{a1} O1W 2 403(2)$	$B_{a1} O4(iii) 2.655(6)$
Cal $O2D 2 345(4)$	C3A C4A 1 365(10)	Cal O18 2 485(2)	Bal O1 2 676(7)
Cal O2D 2.3 $+3(+)$	$C_{3}C_{4}C_{4}C_{1}382(8)$	Ca1 O1D 2.403(2) Ca1 O1A(i) 2 488(2)	Ba1 O3(ii) 2.698(8)
Cal O1B 2 $363(4)$	$C_{3D}C_{4D} = 1.502(0)$	Ca1 OTR(1) 2.400(2) Ca1 O2B 2 545(3)	Ba1 O2(i) 2.000(0) Ba1 O2(i) 2.711(7)
Cal $O2C 2 399(4)$	$C_{3B}C_{4B} = 1.402(0)$	Cal $O2B 2.545(3)$	Ba1 O1(iii) 2.840(7)
Cal O1A $3.014(8)$	C3T N1T + 38(2)	Cal OlA(i) 2.372(2)	Ba1 O2(iii) 2.886(7)
Cal C1A 3.064(7)	$C_{3U}N_{1U} 1.36(2)$	Cal $O2A(i) 2.360(2)$	Bal O4(ii) 2.933(6)
Ca1 Ca2 3.6142(13)	C3V N1V 1.42(2)	C1 O2 1.252(3)	C1 O2 1.233(13)
Ca1 Ca3 3.8772(16)	C4A C5A 1.382(10)	C1 O1 1.258(3)	C1 O1 1.273(12)
Ca2 O6A 2.328(4)	C4C C5C 1.385(8)	C1 C2 1.507(4)	C1 C2 1.515(13)
Ca2 O1T 2.332(5)	C4D C5D 1.392(9)	C2 C4 1.394(4)	C1 Ba1 3.172(10)
Ca2 O1D 2.342(4)	C4B C5B 1.400(8)	C2 C3 1.395(4)	C2 C3 1.373(14)
Ca2 O3A 2.345(5)	C5A C6A 1.391(9)	C2C O1C 1.235(5)	C2 C7 1.395(14)
Ca2 O2C 2.368(4)	C5A C8A 1.491(9)	C2C N3C 1.316(5)	C2C N3C 1.192(18)
Ca2 O1B 2.401(4)	C5C C6C 1.387(8)	C4C N3C 1.407(7)	C2C O1C 1.60(4)
Ca2 O4A 3.002(8)	C5C C8C 1.489(7)	C5 O3 1.257(4)	C3 C4 1.408(15)
Ca3 O1A 2.235(6)	C5D C6D 1.421(9)	C5 O4 1.257(4)	C4 N1 1.348(15)
Ca3 O1S 2.280(7)	C5D C8D 1.483(8)	C5 C6 1.499(4)	C4 C5 1.385(14)
Ca3 O1C 2.380(4)	C5B C6B 1.399(8)	C5C N3C 1.467(7)	C4C N3C 1.362(19)
Ca3 O2B 2.385(4)	C5B C8B 1.483(7)	C6 C8 1.389(4)	C5 C6 1.385(15)
Ca3 O4A(i) 2.236(5)	C6A C7A 1.384(9)	C6 C7 1.391(4)	C5 C8 1.509(13)
Ca3 O5A 2.544(4)	C6C C7C 1.395(8)		C5C N3C 1.311(16)
Ca3 O6A(1) 2.548(3)	C6D C7D 1.396(8)		C6 C7 1.378(16)
CIA OIA 1.229(9)	C6B C/B 1.391(8)		$C_8 O_3 1.267(13)$
C1A O2A 1.246(10)	C8A C10A 1.380(9)		C8 04 1.2/1(12)
C1A C2A 1.481(9)	C8A C9A 1.395(10)		
C1C 01C 1.247(7) C1C 02C 1 276(7)	$C_{SD}C_{SD}C_{SD}(7)$		
C1C C2C 1.270(7)	$C_{8}^{0}C_{9}^{0}D = 1.392(8)$		
C1D O2D 1 232(8)	$C_{3}C_{3}C_{3}C_{1}C_{1}C_{1}C_{1}C_{1}C_{1}C_{1}C_{1$		
C1D O1D 1 236(8)	C12A C13A 1 481(8)		
C1D C2D 1 544(7)	C13A C18A 1 364(10)		
C1B O1B 1.272(7)	C13A C14A 1.399(10)		
C1B C2B 1.511(7)	C14A C15A 1.394(9)		
C1S O1S 1.198(11)	C15A C16A 1.370(9)		
C1S N1S 1.384(19)	C16A C17A 1.399(11)		
C1T O1T 1.183(13)	C16A C19A 1.519(9)		
C1T N1T 1.186(14)	C17A C18A 1.369(11)		
C1U O1U 1.21(3)	C19A O3A 1.196(10)		
C1U N1U 1.30(3)	C19A O4A 1.235(10)		
C1V O1V 1.151(14)	C20A C21A 1.479(8)		
C1V N1V 1.271(14)	C21A C26A 1.382(10)		
C2A C3A 1.370(11)	C21A C22A 1.408(10)		
C2A C7A 1.389(9)	C22A C23A 1.401(8)		
C2C C7C 1.375(8)	C23A C24A 1.400(8)		
C2C C3C 1.391(8)	C24A C25A 1.386(8)		
C2D C3D 1.339(10)	C24A C27A 1.499(7)		
C2D C/D 1.38/(9)	C25A C26A 1.393(8)		
C2B C7B 1.379(8)	$C_2/A USA 1.201(/)$		
C2B C3B 1.386(8)	N1V C2V 1.38(2)		
	$\frac{1}{10} C_{25} \frac{1.4}{0} \frac{1}{10}$		
	1115 (35 1.491(18)		l

 $\begin{array}{l} \text{Symmetries} = \text{Compound 1: (i) } -y + 1/3, \ x - y + 2/3, \ z - 1/3. \ /// \ \text{Compound 2: (i) } -x, \ y - 1/2, \ -z + 3/2. \ /// \ \text{Compound 3: (i) } -y + 3, \ x - y + 1, \ z - 2/3; \ (ii) \ x + 1, \ y + 1, \ z; \ (iii) \ -x + y + 2, \ -x + 3, \ z - 1/3. \end{array}$

Table S2. Selected angles (°) for compound 1.

O5A Ca1 O1V 91.59(16)	O3A Ca2 O2C 88.5(2)	O1C C1C C2C 118.7(5)	C14A C13A C12A 119.3(6)
O5A Ca1 O2D 84.06(15)	O6A Ca2 O1B 106.89(14)	O2C C1C C2C 117.3(5)	C15A C14A C13A 120.4(6)
O1V Ca1 O2D 83.9(2)	O1T Ca2 O1B 160.72(17)	O1C C1C Ca1 80.4(3)	C16A C15A C14A 120.2(6)
O5A Ca1 O2A 103 0(2)	$O1D C_{2} O1B 93 41(16)$	$O_{1}^{2}C$	C15A C16A C17A 119 1(6)
$O_{1V} C_{c1} O_{2A} e_{7} 1(2)$	$O_{2A} C_{2} O_{1B} O_{2} 1(2)$	$C_{2C} C_{1C} C_{21} (5)$	$C_{15A} C_{16A} C_{10A} 120.8(6)$
OIV Cal O2A 87.1(2)	OSA Ca2 OIB 95.1(2)	$C_{2}C_{1}C_{1}C_{1}C_{1}C_{1}C_{1}C_{1}C_{1$	CI3A CI6A CI9A 120.8(6)
O2D Ca1 O2A 168.7(2)	O2C Ca2 O1B 74.41(14)	O2D C1D O1D 126.9(5)	C17A C16A C19A 120.1(6)
O5A Ca1 O1B 168.23(15)	O6A Ca2 O4A 67.72(15)	O2D C1D C2D 117.0(6)	C18A C17A C16A 119.9(6)
O1V Ca1 O1B 86.28(17)	O1T Ca2 O4A 114.7(2)	O1D C1D C2D 116.1(6)	C13A C18A C17A 122.0(7)
$O^{2}D$ C ₃ 1 O1B 84 20(16)	$01DC_{2}204A14581(16)$	O1B C1B C2B 117 8(5)	O3A C19A O4A 122 7(8)
O2D Cal O1D 04.20(10)	$O_{2A} C_{2} O_{4A} 45 O(2)$	$O_{1D} C_{1D} C_{2D} 117.0(3)$	$O_{2A} C_{10A} C_{16A} 118 2(7)$
02A Cal OIB 88.4(2)	05A Ca2 04A 45.0(2)	OIB CIB Ca2 44.0(3)	05A C19A C10A 118.5(7)
OSA Cal O2C 107.19(14)	O2C Ca2 O4A 123.13(16)	C2B C1B Ca2 157.2(4)	04A CI9A CI6A 118.9(8)
O1V Ca1 O2C 160.81(17)	O1B Ca2 O4A 77.45(19)	O1S C1S N1S 137.9(19)	O3A C19A Ca2 45.6(4)
O2D Ca1 O2C 93.98(16)	O6A Ca2 C19A 86.53(17)	O1T C1T N1T 142.5(19)	O4A C19A Ca2 77.3(5)
O2A Cal O2C 92 3(2)	O1T C ₂ 2 C19A 101 3(2)	O1U C1U N1U 118 2(19)	C16A C19A Ca2 163 8(5)
$O1B C_{21} O2C 74 54(14)$	$O1D C_{2} C_{10} A 160 A(2)$	O1V C1V N1V 136 O(18)	$C_{26A} C_{21A} C_{22A} 110 5(5)$
01B Cal 02C 74.54(14)	OID Ca2 CI3A 109.4(2)	G_{1}^{0} G_{2}^{0} G_{2	C20A C21A C22A 119.5(5)
OSA Cal OIA 67.58(15)	03A Ca2 C19A 21.4(2)	C3A C2A C7A 118.9(6)	C26A C21A C20A 121.3(6)
OIV Cal OIA 114.7(2)	O2C Ca2 C19A 104.84(17)	C3A C2A C1A 119.7(6)	C22A C21A C20A 119.2(6)
O2D Ca1 O1A 145.62(16)	O1B Ca2 C19A 84.42(18)	C7A C2A C1A 121.3(6)	C23A C22A C21A 120.2(6)
O2A Ca1 O1A 45.3(2)	O4A Ca2 C19A 23.67(19)	C7C C2C C3C 118.5(5)	C24A C23A C22A 118.8(6)
$O1B C_{21} O1A 123 72(16)$	$O6A C_{2} C_{1} C_{1} B 85 42(14)$	C7C $C2C$ $C1C$ 120 $2(5)$	$C_{25A} C_{24A} C_{23A} 1210(5)$
O1D Cal O1A 125.72(10)	$O_{1T} C_{-2} C_{1D} 177 24(17)$	$C_{2}^{2}C_{2}^{2}C_{2}^{2}C_{1}^{2}C_{1}^{2}C_{1}^{2}C_{2}^{2}C_{2}^{2}C_{1}^{2}C_{1}^{2}C_{1}^{2}C_{2}^{2}C_{2}^{2}C_{2}^{2}C_{1}^{2}C_{1}^{2}C_{2}^{2}C_{2}^{2}C_{2}^{2}C_{1}^{2}C_{1}^{2}C_{2}^{2}C$	C_{25}^{-1}
02C Cal OIA 77.23(18)	011 Ca2 C1B 177.34(17)	C3C C2C C1C 121.3(5)	C25A C24A C27A 120.1(5)
OSA Cal CIA 85.94(17)	OID Ca2 CIB 95.32(16)	C3D C2D C7D 120.2(5)	C23A C24A C27A 118.9(5)
O1V Ca1 C1A 101.4(2)	O3A Ca2 C1B 94.1(2)	C3D C2D C1D 121.0(6)	C24A C25A C26A 119.5(6)
O2D Ca1 C1A 168.8(2)	O2C Ca2 C1B 96.24(14)	C7D C2D C1D 118.8(6)	C21A C26A C25A 120.8(6)
O2A Ca1 C1A 22 0(2)	O1B Ca2 C1B 21 83(14)	C7B C2B C3B 119 5(5)	O5A C27A C24A 118 5(5)
$O1B C_{21} C1A 105 83(17)$	$O_{1A} C_{22} C_{1B} G_{4} A_{0}(18)$	C7B C2B C1B 110 0(5)	$051 C271 C_{2} 61 3(3)$
OID Cal CIA 103.83(17)	O4A Ca2 CIB 04.49(10)	C7D C2D C1D 119.9(3)	$O_{3A} C_{27A} C_{33} O_{1.3}(3)$
02C Cal CIA 84.18(18)	C19A Ca2 C1B /8.85(19)	C3B C2B C1B 120.6(5)	C24A C2/A Ca3 1/9.2(4)
O1A Ca1 C1A 23.31(18)	O6A Ca2 Ca1 134.14(11)	C4A C3A C2A 121.1(6)	C1T N1T C3T 142(2)
O5A Ca1 C1C 85.41(14)	O1T Ca2 Ca1 121.99(15)	C4C C3C C2C 121.0(5)	C1T N1T C2T 108.4(17)
O1V Ca1 C1C 176.96(17)	O1D Ca2 Ca1 71.17(12)	C2D C3D C4D 121.9(6)	C3T N1T C2T 109.5(15)
O2D Ca1 C1C 95 28(16)	O3A Ca2 Ca1 108 7(2)	C2B C3B C4B 120 5(5)	C1U N1U C3U 113 6(18)
O2D Cal CIC $93.20(10)$	$O_{2}C_{2}C_{2}C_{2}C_{1}(100.7(2))$	$C_{2D} C_{3D} C_{4D} 120.5(3)$	C_{111} NIU C_{211} 121(2)
02A Cal CIC 94.0(2)	020 Ca2 Ca1 41.02(9)	C3A C4A C5A 121.3(7)	C10 N10 C20 121(2)
OIB Cal CIC 96.55(14)	OIB Ca2 Ca1 $40.27(10)$	C3C C4C C5C 120.2(5)	C3U NIU C2U 126(2)
O2C Ca1 C1C 22.04(14)	O4A Ca2 Ca1 114.81(16)	C5D C4D C3D 119.5(6)	C1V N1V C2V 115.4(18)
O1A Ca1 C1C 64.56(18)	C19A Ca2 Ca1 112.47(14)	C3B C4B C5B 120.1(5)	C1V N1V C3V 137(2)
C1A Ca1 C1C 78.90(18)	C1B Ca2 Ca1 60 12(10)	C4A C5A C6A 117 5(6)	C2V N1V C3V 107.6(18)
$O5A C_{21} C_{22} 134 24(11)$	$O1A C_{23} O1S 94 2(7)$	$C_{AA} C_{5A} C_{8A} 122 4(6)$	$C_{1A} O_{1A} C_{23} 168 2(7)$
O_{3}^{-1} Cal Cal 137.24(11)	$O1A C_{2} O1C P2 2(2)$	C = 1 C =	$C_{1A} O_{1A} C_{-1} O_{-1} $
01v Cal Ca2 122.11(16)	01A Cas 01C 83.3(2)	C6A C5A C8A 120.0(6)	CIA OIA Cal 80.6(5)
O2D Ca1 Ca2 71.35(12)	OIS Ca3 OIC 81.8(2)	C4C C5C C6C 119.2(5)	Ca3 OIA Ca1 94.0(2)
O2A Ca1 Ca2 108.2(2)	O1A Ca3 O2B 98.6(2)	C4C C5C C8C 120.7(5)	C1C O1C Ca3 132.3(4)
O1B Ca1 Ca2 41.06(10)	O1S Ca3 O2B 80.5(2)	C6C C5C C8C 120.0(5)	C1D O1D Ca2 131.2(4)
O2C Ca1 Ca2 40 38(10)	O1C Ca3 O2B 162 24(14)	C4D C5D C6D 118 6(5)	C1B O1B Ca1 137 1(3)
$O1A C_{21} C_{22} 114 90(15)$	$O1A C_{23} O5A 78 2(2)$	C4D C5D C8D 121 2(5)	$C1B O1B C_{2}2 113 6(3)$
OIA Cal Ca2 II4.90(15)	OIA Cas OSA 154.7(2)	C4D C5D C8D 121.2(5)	C = 1 O D C = 2 O O (0(14))
CIA Cal Ca2 112.8/(14)	015 Ca3 05A 154.7(2)	C6D C5D C8D 120.3(5)	Cal OIB Ca2 98.68(14)
CIC Cal Ca2 60.15(10)	OIC Ca3 O5A 73.41(14)	C6B C5B C4B 118.7(5)	CIS OIS Ca3 177.1(18)
O5A Ca1 Ca3 39.26(9)	O2B Ca3 O5A 124.32(14)	C6B C5B C8B 120.4(5)	C1T O1T Ca2 138.3(9)
O1V Ca1 Ca3 121.71(16)	O1A Ca3 C27A 84.6(3)	C4B C5B C8B 120.8(5)	C1V O1V Ca1 137.3(9)
O2D Ca1 Ca3 110.68(12)	O1S Ca3 C27A 178.6(6)	C7A C6A C5A 121.2(6)	C1A O2A Ca1 113.0(5)
$O_{2A} C_{21} C_{23} 70.00(10)$	$O1C C_{23} C_{27} A 08 O1(15)$	$C_{5}C_{6}C_{6}C_{7}C_{110}0(5)$	$C_{1}C_{0}C_{0}C_{0}C_{1}C_{1}C_{0}C_{0}C_{0}C_{0}C_{0}C_{0}C_{0}C_{0$
$O_{2A} Cal Ca_{3} 79.90(19)$	O1C CaS C27A 98.91(15)	$C_{7} C_{7} C_{7$	C1C O2C Ca2 130.1(3)
OIB Cal Ca3 148.62(11)	O_{2B} Ca3 C2/A 98.85(15)	C/D C6D C5D 119.7(6)	CIC 02C Cal 113.1(3)
O2C Ca1 Ca3 76.91(10)	O5A Ca3 C27A 25.76(14)	C7B C6B C5B 120.4(5)	Ca2 O2C Ca1 98.60(14)
O1A Ca1 Ca3 35.10(10)	O1A Ca3 Ca1 50.9(2)	C6A C7A C2A 119.8(6)	C1D O2D Ca1 130.8(4)
C1A Ca1 Ca3 58.15(15)	O1S Ca3 Ca1 123.2(4)	C2C C7C C6C 121.0(5)	C19A O3A Ca2 113.0(5)
$C1C C_{21} C_{23} 55 87(10)$	$O1C C_{23} C_{21} 54 72(10)$	$C^{2}D$ $C^{7}D$ $C^{6}D$ 120 1(6)	$C194 O44 C_{2} 79 O(5)$
$C_{2} C_{2} C_{2$	$O2D C_{a2} C_{a1} 128 58(11)$	C2D C7D C0D 120.1(0)	$C_{27A} O_{5A} C_{c1} 122 f(4)$
Ca2 Ca1 Ca5 115.95(4)	02B Cas Cal 158.58(11)	C2B C7B C0B 120.0(3)	C27A OSA Cal 155.0(4)
U6A Ca2 O1T 91.92(16)	USA Ca3 Ca1 35.38(9)	C10A C8A C9A 119.4(6)	C2/A O5A Ca3 93.0(3)
O6A Ca2 O1D 84.18(16)	C27A Ca3 Ca1 56.59(11)	C10A C8A C5A 121.0(6)	Ca1 O5A Ca3 105.36(14)
O1T Ca2 O1D 84.2(2)	O1A C1A O2A 121.1(7)	C9A C8A C5A 119.6(6)	C1S N1S C2S 138.4(16)
O6A Ca2 O3A 102 6(2)	O1A C1A C2A 121 0(7)	C9C C8C C5C 119 8(5)	C1S N1S C3S 109 2(14)
$O1T C_{2} O3A 867(2)$	O2A C1A C2A 117 9(7)	C9D C8D C5D 119 8(5)	C2S N1S C3S 112 2(17)
$O_{1} C_{a2} O_{2} A_{1} C_{a} O_{2} A_{1} C_{$	$O_{1A} O_{1A} O_{-1} T (17)$	COD COD COD 117.0(3)	C25 1115 C35 112.2(17)
01D Ca2 OSA 168.8(2)	OIA CIA Cai / 0.1(5)	CAR COR COR 119.0(2)	
O6A Ca2 O2C 168.61(15)	O2A CIA Ca1 45.0(4)	C11A C12A C13A 120.2(6)	
O1T Ca2 O2C 86.32(16)	C2A C1A Ca1 162.9(5)	C18A C13A C14A 118.2(6)	
O1D Ca2 O2C 84.45(16)	O1C C1C O2C 124.0(5)	C18A C13A C12A 122.0(6)	

2	3
O1C Ca1 O1W 109.30(9)	O1C Ba1 O4 89.7(3)
O1C Ca1 O3 83.94(9)	O1C Ba1 O1 93.9(3)
O1W Ca1 O3 151.58(8)	O4 Ba1 O1 90.09(19)
O1C Ca1 O1 154.85(8)	O1C Ba1 O3 86.9(3)
O1W Ca1 O1 85.26(8)	O4 Ba1 O3 146.6(2)
O3 Ca1 O1 74.64(8)	O1 Ba1 O3 123.3(2)
O1C Ca1 O4 81.15(9)	O1C Ba1 O2 95.8(3)
O1W Ca1 O4 152.59(8)	O4 Ba1 O2 68.7(2)
O3 Ca1 O4 51.63(8)	O1 Ba1 O2 156.6(2)
O1 Ca1 O4 95.26(9)	O3 Ba1 O2 78.6(2)
O1C Ca1 O2 147.73(8)	O1C Ba1 O1 165.3(3)
O1W Ca1 O2 84.67(8)	O4 Ba1 O1 78.6(2)
O3 Ca1 O2 97.32(8)	O1 Ba1 O1 95.11(8)
O1 Ca1 O2 50.70(7)	O3 Ba1 O1 97.8(3)
O4 Ca1 O2 74.84(8)	O2 Ba1 O1 71.7(2)
O1C Ca1 C5 83.33(9)	O1C Ba1 O2 149.4(3)
O1W Ca1 C5 167.36(8)	O4 Ba1 O2 116.2(2)
O3 Ca1 C5 25.82(8)	O1 Ba1 O2 71.5(2)
OI Cal C5 82.99(8)	O3 Ba1 O2 79.8(3)
O4 Cal C5 25.90(8)	O2 Bal O2 108.25(18)
O2 Cal C5 84.30(8)	OI Bal O2 45.26(19)
OIC Cal CI 161.29(8)	OIC Bal 04 88.2(3)
01W Cal CI 88.88(8)	O4 Bal O4 $166.4(2)$
$O_3 Cal Cl 81.69(8)$	OI Bal O4 $/6.66(19)$
OI Cal CI 25.75(7)	$O_{2} B_{a1} O_{4} 40.0(2)$
$O_4 Cal C1 80.55(9)$	O_2 Dat O_4 124.9(2) O1 Pa1 O4 105 3(2)
$C_{2} C_{21} C_{1} C_{2} C_{3} C_{1} C_{1} C_{2} C_{3} C_{$	$O_{1} B_{a1} O_{4} G_{2} T_{1}(19)$
$O_{2} C_{1} O_{1} 121 7(2)$	$O_{1}C B_{2}1 C_{1} 169 3(3)$
$O_2 C_1 C_2 119 5(2)$	O4 Ba1 C1 100.9(2)
01 C1 C2 118 7(2)	O1 Ba1 C1 87 3(2)
$O_2 C_1 C_{a1} 65.41(14)$	$O_3 Ba1 C1 83.6(3)$
O1 C1 Ca1 59.12(14)	$O_2 C_1 O_1 123.2(9)$
C2 C1 Ca1 160.27(18)	O2 C1 C2 119.6(8)
C4 C2 C3 119.6(3)	O1 C1 C2 117.2(9)
C4 C2 C1 120.0(2)	C3 C2 C7 118.9(10)
C3 C2 C1 120.4(2)	C3 C2 C1 120.6(9)
O1C C2C N3C 126.1(4)	C7 C2 C1 120.4(9)
O3 C5 O4 121.2(3)	N3C C2C O1C 109(3)
O3 C5 C6 119.0(3)	C2 C3 C4 122.5(10)
O4 C5 C6 119.8(3)	N1 C4 C5 123.1(10)
O3 C5 Ca1 59.42(16)	N1 C4 C3 118.7(10)
O4 C5 Ca1 62.18(16)	C5 C4 C3 118.1(10)
C6 C5 Ca1 174.6(2)	C6 C5 C4 118.7(10)
C8 C6 C7 119.3(3)	C6 C5 C8 120.2(9)
C8 C6 C5 120.2(3)	C4 C5 C8 121.1(10)
C/ C6 C5 120.5(3)	C7 C6 C5 123.0(10)
C2C N3C C4C 121.9(4)	$C_{6}C_{7}C_{2}118.5(10)$
C4C N3C C5C 11(0(4)	$03 \ C8 \ O4 \ 123.8(9)$
$C_{1} = C_{1} = C_{2} = C_{2$	$O_{3} C_{6} C_{5} 118.2(9)$
$C_1 \cup I \cup C_{11} = 3.13(10)$	C2C N3C C5C 128(2)
$C_{1} O_{2} C_{2} I_{3} R_{2} R_{2$	$C_{2}C_{113}C_{12}C_{1$
$C_1 O_2 C_{a1} 00.09(10)$ $C_5 O_3 C_{a1} 94 76(18)$	C5C N3C C4C 108 6(16)
C5 O4 Ca1 91.92(19)	C1 O1 Ba1 166.1(7)

Table S3. Selected angles (°) for compounds 2 and 3.

S4. PXRD data refinement

Pattern-matching analyses of the diffractograms were done by means of the FULLPROF program (pattern-matching analysis)¹ on the basis of the space group and the cell parameters found for single crystal X-ray diffraction.



Figure S7. Pattern-matching refinement of PXRD data of compound 1.

¹ (a) Rodríguez-Carvajal, J. FULLPROF, Program Rietveld for Pattern Matching Analysis of Powder Patterns; Abstacts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr: Toulouse, France, 1990, 127. (b) Rodríguez-Carvajal, J. FULLPROF 2000, version 2.5d; Laboratoire Léon Brillouin (CEA-CNRS), Centre d'Études de Saclay, Gif sur Yvette Cedex: France, 2003.



Weight Loss (%) $\Delta m \sim 38\%$ (DMF loss) Temperature (°C) Figure S10. TGA curve of compound 1. $\Delta m \sim 16\%$ (water loss) Weight Loss (%) $\Delta m \sim 19\%$ (DMF loss) Temperature (°C)

S5. Thermogravimetric analyses under N₂ flow

Figure S11. TGA curve of compound 2.



Table S4. Experimental and expected values of solvent loss for compounds 1–3.

	Experimental loss of solvent (%)	Expected loss of solvent (%)
Compound 1	38	42
Compound 2	35	38
Compound 3	19	19

S6. N₂ adsorption-desorption isotherms at -196 °C



Figure S13. N₂ adsorption-desorption isotherms at 77 K for compounds 1–3. Full symbols correspond to adsorption branch and empty symbols correspond to desorption branch.

In view of the negligible N_2 adsorption shown by all compounds, various attempts were made to replace DMF molecules present in the crystal structures by other more volatile solvents, such as methanol, tetrahydrofuran or dichloromethane that could be easily removed by thermal treatment. However, the crystalline structure was drastically modified for the three compounds after solvent exchange process as confirmed by PXRD data (see Figure S14).



Figure S14. PXRD diffractograms of compounds 1–3 after various solvent exchanges.

S7. Photoluminescence properties



Figure S15. (a) Excitation and (b) emission spectra for btb, bdc, and NH₂-bdc free ligands under $\lambda_{ex} = 325$ nm at room temperature.



Figure S16. Emission spectra at room and low temperature for (a) H_3 btb, (b) H_2 bdc, and (c) NH_2 - H_2 bdc under 325 nm excitation wavelength.

• PL spectra of compounds 1–3:



Figure S17. Solid state emission spectra for compounds 1–3 at room temperature upon excitation at 330 nm.



Figure S18. Excitation spectra for compounds 1-3 at their maxima emission wavelength recorded at 10 K.

• Micro-PL images of compounds 1–3:

Compounds 1-3 show blue, green and red emissions when excited in steady-state at 365, 435, and 546 nm wavelengths (as shown Figures S16–18) in good agreement with their wide emission bands covering the visible spectrum (see Figure14), which means that their emission composes of different colors. Bearing in mind that the emission spectra of these compounds always corresponds to that region above the excitation wavelength, as the excitation wavelength shifts towards red, the emission recorded contains only the less energetic region of the visible spectrum above the excitation wavelength, which delimits the resulting overall color. Thus, under excitation with UV

light (365 nm in the photographs or 325 nm in the spectra), the main emission is blue colored in agreement with the emission maxima observed in the 370-481 nm. However, exciting the sample at 435 nm, the emission spectrum lacks the blue region and only the less energetic tail (450–700 nm region) is observed, which accounts for the representative green color. The same occurs for the red emission achieved when exciting the single crystal at 546 nm, where the spectrum collected would be that corresponding to ca. 560–700 nm range, that is, red emission. Although it is true that the emission intensity of all compounds at that region (546–700 nm) is quite low, the high power of the Hg lamp employed along with the microscope allows measuring it.

In terms of emission capacity, the following trend may be concluded in line with the brightness shown at selected excitation wavelengths: 1 > 3 > 2. The trend is in good agreement with the comparative intensity of the signal emitted by the compounds (as shown in spectra of Figure 9 of the manuscript) taking into account that all measurements have been performed under the same experimental conditions. The same effect is also reflected in the excitation spectra (see Figure S19).



Figure S19. Micro-PL images of compound 1 under excitation at different monochromatic lights.



Figure S20. Micro-PL images of compound 2 under excitation at different monochromatic lights.



Figure S21. Micro-PL images of compound 3 under excitation at different monochromatic lights.

• Emission decay curves of ligands and compounds 1–3:

Emission decay curves were measured at 10 K over polycrystalline samples of H₃btb, H₂bdc, and NH₂-H₂bdc as well as compounds **1–3** at selected emission wavelengths under monochromatic excitation($\lambda = 325$ nm). The curve for each ligand has been recorded with same setting and conditions of the corresponding compound.



Figure S22. Decay curves for (a) H₃btb, (b) H₂bdc, and (c) NH₂-H₂bdc under $\lambda_{ex} = 325$ nm excitation and selected emission wavelength.

In the emission region below or close to the band maxima, decay curves were not fitted since their lifetimes are below 10 μ s, thus associated to fluorescent processes, so they cannot be distinguished from the pulse of the lamp itself. Instead, decay curves recorded for higher wavelengths showed multiexponential shapes, attributed to several processes with different lifetimes. These decay curves were recorded employing different exposure times in order to achieve 10^4 counts in the pulse of reference. On the other hand, variable window sizes (i.e. elapsed time ranges) were employed for each compound and selected emission wavelength according to the intensity and decay time of the phosphorescent signal. Best fitting results can be found in Table 1 of the manuscript.



Figure S23. Phosphorescent decay curves for compound 1 at selected emission wavelengths recorded at 10 K.







Figure S24. Phosphorescent decay curves for compound 2 at selected emission wavelengths recorded at 10 K.



Figure S25. Phosphorescent decay curves for compound 3 at selected emission wavelengths recorded at 10 K.

Additionally, variable-temperature decay curves were recorded for compound 2 at the emission wavelength associated with the longest lifetime (450 nm). As shown in Table 2, the longest lifetime is stable up to 150 K and slowly decreases with rising the temperature.





Figure S26. Phosphorescent decay curves for compound 2 at $\lambda_{em} = 450$ nm recorded at variable temperatures.

• Time-resolved emission spectra for compounds 1–3:

TRES were measured for compounds 1-3 covering the whole emission bands with a step of 10 nm and 0.2 Hz or 1 Hz of frequency at the pulsed lamp for 1 and 2 or 3, respectively. A band pass of 5 nm and 2.5 nm was fixed for the excitation and emission monochromator slits.



Figure S27. Time-resolved emission spectra of compound 1 at 10 K at selected times after the excitation source: (a) between 0 and 95 ms and (b) between 200 and 4000 ms.



Figure S28. Time-resolved emission spectra of compound 3 at 10 K at selected times after the excitation source: (a) between 0 and 95 ms and (b) between 200 and 4000 ms.

S8. TD-DFT calculations

Ligand molecules were taken from the X-ray single crystal crystallographic coordinates of compounds 1–3 (Figure S29).



Figure S29.	Models of	ligand	molecules	used for	the c	calculations.
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Calcd. λ (nm)	Calcd. band λ (nm)	Exp. λ (nm)	Significant contributions / osc. st. $[a]$
		btb	
378 386	385	390	HOMO – 1 → LUMO (99%) / 0.124 HOMO – 1 → LUMO (100%) / 0.095
		bdc	
407 408	401	380	HOMO – 1 → LUMO (99%) / 0.079 HOMO – 1 → LUMO (100%) / 0.062
		NH ₂ -bdc	
452			HOMO \rightarrow LUMO (97%) / 0.065
507	535	550	HOMO → LUMO (98%) / 0.091
543			HOMO \rightarrow LUMO (99%) / 0.102

Table S4. TD-DFT calculated	main emission	energies (nm)	and electronic	transitions of all
ligands.				

[a] Oscillator strengths.



НОМО



Figure S30. Highly Occupied and Lowest Unoccupied Molecular Orbitals involved in the main luminescent charge transitions.

S9. Calculation of the lowest-lying triplet states (T₁)

The T_1 - S_0 energy difference, which corresponds to the main phosphorescencent emission line, has been estimated from vertical excitation performed for the optimized geometry of the lowest lying excited triplet state (T_1). The triplet state geometry optimization and frequencies calculation was performed on suitable models of ligand structures (Figure S15) by Gaussian 09 package, using the Becke three parameter hybrid functional with the non-local correlation functional of Lee-Yang-Parr (B3LYP) with the 6-31G++(d,p) basis set for all atoms.

Figure S31. Highest Occupied (single-occupied alpha) and Lowest Unoccupied Molecular Orbitals of the first excited triplet state.