Electronic Supplementary Information for:

**A luminescent MOF based on pyrimidine-4,6-dicarboxylate ligand and lead(II) with unprecedented topology**

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**S1. Additional structural details.**

Imagen que contiene Patrón de fondo

Descripción generada automáticamente

**Figure S** Packing of compound **1** along the *c* axis viewing direction.

Imagen que contiene Patrón de fondo

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**Figure S** Packing of compound **1** along the *a* axis viewing direction.

**S2. Continuous Shape Measurements (CShMs).**

**Table S1.** Continuous Shape Measurements for the coordination environments for compound **1**. The lowest SHAPE values are shown in bold blue, indicating best fits.

**Codes:**

HP-7 1 D7h Heptagon

HPY-7 2 C6v  Hexagonal pyramid

PBPY-7 3 D5h Pentagonal bipyramid

COC-7 4 C3v Capped octahedron

CTPR-7 5 C2v Capped trigonal prism

JPBPY-7 6 D5h Johnson pentagonal bipyramid J13

JETPY-7 7 C3v Johnson elongated triangular pyramid J7

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| **Structure [ML7]** | **HP-7** | **HPY-7** | **PBPY-7** | **COC-7** | **CTPR-7** | **JPBPY-7** | **JETPY-7** |
| **Pb1** | 32.503 | 19.509 | 5.861 | 2.872 | **2.159** | 9.258 | 20.855 |

**Codes:**

OP-8 1 D8h Octagon

HPY-8 2 C7v Heptagonal pyramid

HBPY-8 3 D6h Hexagonal bipyramid

CU-8 4 Oh Cube

SAPR-8 5 D4d  Square antiprism

TDD-8 6 D2d Triangular dodecahedron

JGBF-8 7 D2d Johnson gyrobifastigium J26

JETBPY-8 8 D3h Johnson elongated triangular bipyramid J14

JBTPR-8 9 C2v Biaugmented trigonal prism J50

BTPR-8 10 C2v Biaugmented trigonal prism

JSD-8 11 D2d Snub diphenoid J84

TT-8 12 Td Triakis tetrahedron

ETBPY-8 13 D3h Elongated trigonal bipyramid

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| **Structure [ML8]** | **OP-8** | **HPY-8** | **HBPY-8** | **CU-8** | **SAPR-8** | **TDD-8** | **JGBF-8** |
| **Pb2** | 27.041 | 24.070 | 16.303 | 10.258 | **1.768** | 3.401 | 13.684 |

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| **Structure [ML8]** | **JETBPY-8** | **JBTPR-8** | **BTPR-8** | **JSD-8** | **TT-8** | **ETBPY-8** |
| **Pb2** | 24.012 | 3.876 | 3.624 | 5.445 | 10.587 | 19.375 |

**Codes:**

DP-12 1 D12h Dodecagon

HPY-12 2 C11v Hendecagonal pyramid

DBPY-12 3 D10h Decagonal bipyramid

HPR-12 4 D6h Hexagonal prism

HAPR-12 5 D6d Hexagonal antiprism

TT-12 6 Td Truncated tetrahedron

COC-12 7 Oh Cuboctahedron

ACOC-12 8 D3h Anticuboctahedron J27

IC-12 9 Ih Icosahedron

JSC-12 10 C4v  Johnson square cupola J4

JEPBPY-12 11 D6h Johnson elongated pentagonal bipyramid J16

JBAPPR-12 12 C2v Biaugmented pentagonal prism J53

JSPMC-12 13 Cs Sphenomegacorona J88

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| **Structure [ML12]** | **DP-12** | **HPY-12** | **DBPY-12** | **HPR-12** | **HAPR-12** | **TT-12** | **COC-12** |
| **Pb3** | 31.836 | 28.687 | 19.525 | 10.661 | 17.152 | 11.788 | **1.830** |

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| **Structure [ML12]** | **ACOC-12** | **IC-12** | **JSC-12** | **JEPBPY-12** | **JBAPPR-12** | **JSPMC-12** |
| **Pb3** | 7.325 | 5.604 | 20.646 | 11.573 | 12.422 | 19.913 |

**S3. Powder X-ray Diffraction Analysis.**

Imagen que contiene Gráfico

Descripción generada automáticamente

**Figure S** Pattern-matching analysis of polycrystallinesample of compound **1**.

**S4. FT-IR spectroscopy.**

Infrared spectroscopy was used as an initial characterization technique to check the presence of pmdc in compound **1** (Figure S4). Table S2 shows the wavenumbers of the most relevant bands, together with their relative intensities and the proposed assignation in each case for the compound **1**.

The spectrum of compound **1** shows a broad and intense band in frequency region of 3550-3100 cm-1, assigned to the characteristic peaks of OH vibration of free water molecules and to the C-H vibration of the pyrimidinic ring of the pmdc ligand. The intense vibrations around 1650 cm-1 and 1360 cm-1 correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups. At 1385 cm-1 appears the strong vibration of the nitrate anion, while in the 1300-1000 cm-1 region several medium- and weak-intensity peaks appear that can be attributed to the distortions originated in the aromatic ring of pmdc ligand. The vibration bands of the M-O and M-N bonds are observed below 550 cm-1.

**Table S2.** Main IR absorption bands (cm–1) for the compound **1**.a

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| --- | --- |
| Asig.b | Compound **1** |
| ν (O–H) | 3470m, 3170m |
| ν (C–H) | 3075m |
| νas(O–C–O) + ν (C=C + C=N) | 1635s, 1600s, 1585sh, 1535s |
| ν (Car–C) | 1460w |
| νs (O–C–O) | 1360s, 1305w |
| ν (NO3) | 1385s |
| δip(C–H) | 1285m, 1185m, 1095w, 1040w, 1015m |
| δop(C–H) | 940w |
| δring | 835m |
| δip(O–C–O) | 810m |
| δop(O–C–O) | 730s, 715ss |
| τring | 695m, 670m, 560w |
| ν (M–O + M–N) | 505w, 485w, 445w, 415w |

a vs: very strong, s: strong, m: medium, w: weak, sh: shoulder. b ν: stretching, δ: bending, ip: inside plane, op: out of plane, s: symmetric, as: antisymmetric.

Gráfico, Histograma

Descripción generada automáticamente

**Figure S** Comparison of the FTIR spectra of compound **1** and the free H2pmdc ligand.

**S5. Photoluminescence measurements and calculations.**



**Figure S** Excitation (λem = 435 nm) and emission (λex = 335 nm) spectra of H2pmdc ligand recorded at room temperature.

The emission lifetimes were estimated by measuring the decay curves for both maxima. The signal for the first maximum was so weak and the lifetime quite short so it was estimated by deconvolution. On the contrary, the lifetime of the maximum at 550 nm was estimated by tail fitting procedure and gave two components of 5.71(59) µs with a weight of 40% and a second component of 116.4(34) µs with a weight of 60%.

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**Figure S** Decay curves of the emission of compound **1** at room temperature for the main emission maxima.



**Figure S** Monomeric model taking from the X-ray coordinates used for the calculations of the PL properties of compound **1**.

**Table S3**. Calculated main excitation and emission energies (nm), singlet electronic transitions and associated oscillator strengths of model of compound **1** in gas phase.

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| Exc. state | Calcd. λ (nm) | Significant contributions | Osc. strength (a.u.) |
| Excitation energies | | | |
| 7 | 395 | HOMO – 5 → LUMO (99%) | 0.1421 |
| 10 | 335 | HOMO – 7 → LUMO (99%) | 0.0356 |



**Figure S** Emission spectrum of compound **1** collected at 15 K under monochromatic laser light (λex = 325 nm).



**Figure S** Comparison of the low temperature excitation spectra collected over the two maxima observed in the emission of compound **1**.

The emission lifetimes for the low temperature decay curves were estimated with the same fitting procedure explained for RT measurements by measuring the decay curves for both maxima. The signal for the first maximum was so weak and the lifetime quite short so it was estimated by deconvolution. On the contrary, the lifetime of the maximum at 550 nm was estimated by tail fitting procedure and gave two components of 5.71(59) µs with a weight of 40% and a second component of 116.4(34) µs with a weight of 60%.

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**Figure S** Decay curves of the emission of compound **1** at low temperature for the main emission maxima.



**Figure S** TRES recorded at 15 K for compound **1** showing a selection of spectra.

**S6. Diffuse reflectance.**



**Figure S** Diffuse reflectance spectrum acquired on polycrystalline sample of compound **1**.