A novel 3D porous metal–organic framework based on trinuclear cadmium clusters as a promising luminescent material exhibiting tunable emissions between UV and visible wavelengths

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Syntheses: 2,6-di-(4-triazolyl)pyridine (L) ligand was synthesized using the literature method.\(^\text{S1}\) Compound 1: L (92.4 mg, 0.4 mmol) and Cd(BF\(_4\))\(_2\)•6H\(_2\)O (78.8 mg, 0.2 mmol) were heated under reflux in H\(_2\)O for 2h and then the resulting solution was filtered. Colorless single-crystals suitable for X-ray diffraction were obtained by slow evaporation in glass vial within several days. Yield: 48%. IR (KBr): \(\text{v} = 3446.3\text{m}, 3108.2\text{s}, 2360.5\text{m}, 1611.3\text{s}, 1532.5\text{vs}, 1465.2\text{vs}, 1398.2\text{w}, 1283.3\text{s}, 1253.2\text{m}, 1097.0\text{w}, 1060.6\text{s}, 891.2\text{m}, 807.3\text{s}, 770.8\text{s}, 750.2\text{s}, 628.9\text{s}, 469.4\text{cm}^{-1}\). Anal. (%): found (calc.): C\(_{54}\)H\(_{71}\)B\(_2\)Cd\(_3\)F\(_{14}\)N\(_{42}\)O\(_{15.5}\)Si, C: 30.54 (29.36), H: 3.25 (3.24), N: 26.53 (26.63).

X-ray Crystallography: Crystal data was collected on Bruker SMART 1000 CCD detector with graphite-monochromated Mo-K\(_\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)) at 294(2) K. compound 1, C\(_{54}\)H\(_{71}\)B\(_2\)Cd\(_3\)F\(_{14}\)N\(_{42}\)O\(_{15.5}\)Si, M = 2209.44, Rhombohedral, R-3, \(a = 20.1077(11)\,\text{Å}\), \(b = 20.1077(11)\,\text{Å}\), \(c = 20.234(2)\,\text{Å}\), \(\alpha = 90°\), \(\beta = 90°\), \(\gamma = 120°\), \(V=7085.1(9)\,\text{Å}^3\), \(Z = 3\), \(\mu = 0.787\,\text{mm}^{-1}\), \(Dc = 1.553\,\text{Mg}\,\text{m}^{-3}\), \(F(000) = 3321\), \(R_{\text{int}} = 0.0317\), 13502 reflections, 3224 with \(I > 2\sigma(I)\) for 252 parameters, \(R_1 = 0.0413\) for \(I > 2\sigma(I)\), \(R_1 = 0.0495\) and \(wR_2 = 0.1357\) for all data, \(GOF = 1.009\). The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 \(^{S2}\)and SHELXL-97 programs. \(^{S3}\)

Characterization: Elemental analysis for C, H and N were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were measured with a Bruker Tensor 27 Spectrometer on KBr disks. The fluorescent spectrum was measured on a Varian Cary Eclipse Fluorescence spectrophotometer. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-K\(_\alpha\) radiation. Thermal analyses (under an nitrogen atmosphere, heating rate of 5 °C min\(^{-1}\)) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus.
Figure S1. Topological representation of compound 1 showing a rhombohedral coordination network. The [Cd$_3$L$_{12}$] trinuclear clusters are taken as nodes of the framework.

Figure S2. (a) Hydrogen-bonded interactions of the water molecules and anions without the framework. (b) A perspective view showing the interactions of the water molecules and anions with the MOF along the c axis. Color code: Cd, brown; O, red; SiF$_6^{2-}$, polyhedron, blue; BF$_4^-$, polyhedron, green.
Figure S3. TGA curves of complex 1-5. Color lines: 1, red; 2, green; 3, blue; 4, magenta; 5, orange. The inset pictures represent the TGA curves of complex 6 and 7. Color scheme: 6, dash line, green; 7, dash-dot line, blue.

Figure S4. PXRD patterns of (a) a fresh sample 1 and rehydration sample 7, (b) complexes 2-5, after heat treatment of sample 1.
References