

Supplementary Materials

Experimental

Methods and Instrumentations

Elemental analyses of C, H and N were performed on a PerkinElmer 240C elemental analyzer.

The photoluminescence spectra were obtained from solid films prepared by drop casting a DMF suspension of the complex **1** on quartz plate using a Nanolog spectrofluorometer from HORIBA Jobin Yvon.

X-Ray crystal structure determination

Single crystal X-ray data were collected at 100 K by using the Bruker SMART APEX CCD diffractometer on graphite monochromatic MoK radiation (0.71073). The International Table for X-ray crystallography applied to the linear absorption coefficient, scattering factors for the atoms and anomalous dispersion correction[1]. The data integration and reduction were worked out with SAINT software[2]. For the collected reflections with SADABS[3], empirical absorption correction was applied and the space group was defined using XPREP.

The structure was solved by the direct methods using SHELXTL-2016 and refined on F by full matrix least-squares using the SIR -97 program package[4]. Only a few H atoms could be located in the difference Fourier maps in the structure. The remaining were positioned in calculated positions using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. All non-H atoms were refined anisotropically.

Topology

The topological description of a MOF includes the simplification procedure, i.e. illustration of a network in terms of the graph-theory approach. In the standard simplification procedure metal atoms remain intact, while ligands are represented by their centers of mass keeping the connectivity with their neighbors. The subsequent secondary simplification of the obtained net includes removing of the 0-c and 1-c nodes (extraframework and

terminal structural groups). Therefore, this description characterizes the way of connection of ligands and metal centers.

Computational methodology

All reported computations were performed using ORCA 3.0 computational package [5, 6]. Experimental geometry was obtained from single crystal X-ray data. The single point energy calculation carried out by hybrid B3LYP functional[7] using Aldrich's def2-TZVP basis set for Mo atom, SARC-ZORA-TZVP[8] for the Sm atom, and def2-SVP basis set for C, H, O, N atoms [9-11] to calculate the HOMO and LUMO energies. Relativistic effects were included with the zeroth-order relativistic approximation (ZORA) [8]. To speed up the calculations we employed the resolution of identity (RI) approximation with the decontracted auxiliary def2-SVP/J and def2-TZV/J Coulomb fitting basis sets and the chain-of-spheres (RIJCOSX) approximation to exact exchange as executed in ORCA. DFT calculation utilizes the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ)[12, 13].

Hirshfeld surface were mapped using Crystal Explorer [14] software using crystal structure coordinates of CIF files.

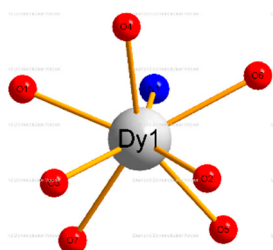


Figure S1. Schematic representation of the distorted square antiprism coordination environment of the Dy(III) metallic center in $[\text{Dy}(\text{DMF})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{Fe}(\text{CN})_5\cdot\text{H}_2\text{O}]$ (**1**).

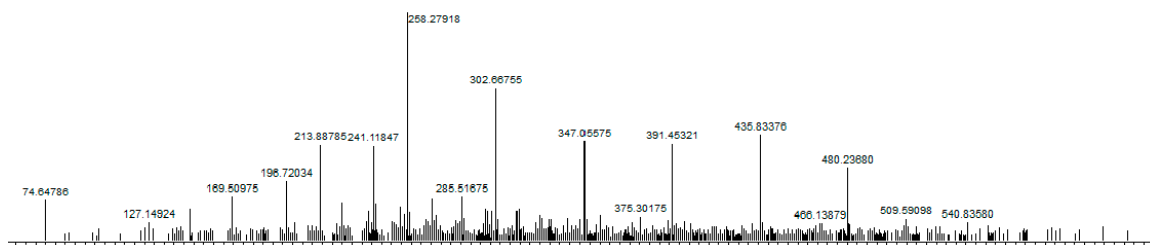


Figure S2. Mass spectrum of complex **1**.

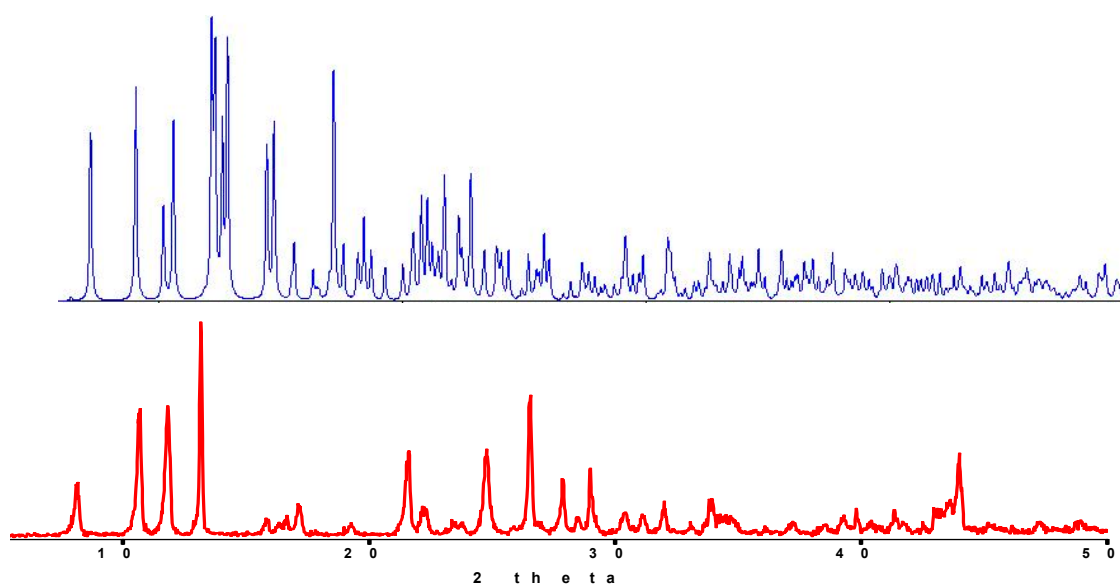


Figure S3. - Powder XRD patterns of simulated (blue, up) from the single-crystal data and powder XRD patterns of experimental (red, down) of the complex **1**.

References

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