Supporting Information

Pure White-Light and Blue-to-Yellow Emission Tuning in Single Crystal of Dy(III) Metal-Organic Framework

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Materials and methods

Solvents were purchased from Alfa Aesar and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. NMR spectra were recorded on Bruker Avance 400 NMR spectrometer. The C, H, and N elemental analyses were measured on a Perkin-Elmer 240 elemental analyzer. The powder X-ray diffraction data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K α , $\lambda = 1.5418$ Å).

Photoluminescence spectra (emission and excitation spectra) were taken on a Horiba Jobin–Yvon IBH FL-322 Fluorolog 3 spectrometer and were corrected for source intensity by standard correction curves. Time-resolved measurements were measured using the multichannel scaling (MCS) single-photon-counting option on the HORIBA Jobin-Yvon IBHFL-322 Fluorolog 3 spectrometer. The quantum yield measurements were performed in quartz sample holder at specific wavelength, and collected emission wavelengths from 400 nm to 800 nm using an absolute quantum yield measurement system (Hamamatsu, Model C11347-11).

Crystallography

The crystals of Dy complex were placed in oil and a colorless block single crystal of dimensions 0.20 \times 0.15 \times 0.12 mm was mounted on a glass fiber and placed in a low-temperature N₂ stream. X-Ray

diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)¹ from reflections taken from tree sets of 12 frames, each at 10s exposure. The structure was solved by Direct methods using the program SHELXS-2013.² The refinement and all further calculations were carried out using SHELXL-2013.³ The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted fullmatrix least-squares on F^2 . A semi-empirical absorption correction was applied using SADABS in APEX2;¹ transmission factors: $T_{min}/T_{max} = 0.6274/0.7458$. The SQUEEZE instruction in PLATON⁴ was applied to remove all disordered solvents. The residual electron density was assigned to one molecule of water per asymmetric unit.

Crystal data for Dy(III)-MOF (complex 1): $C_{30}H_{33}DyN_6O_{12}$, M = 832.12, Orthorhombic, space group $Pna2_1$, a= 15.081(5), b= 16.728(5), c= 13.061(5) Å, alpha=90, beta=90, gamma=90 °, $V= 3295.0(19) Å^3$, Z = 4, $D_c = 1.677$ g cm⁻³, $\mu = 2.340$ mm⁻¹, T = 173 K. Refinement of 8746 parameters converged at final R_1 [for selected data with $I > 2\sigma(I)$] = 0.0481, wR_2 (all data) = 0.0981. CCDC 990178.

Synthesis of ligand



Scheme 1. Molecular structure of the ligand TETP.

1,1',1''-((2,4,6-triethylbenzene-1,3,5 triyl)tris(methylene))tris(pyridin-4(1H)-one) (TETP): Under Ar, 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (2.6 g, 6 mmol) was added to a suspension of 4-hydroxypyridine (1.9 g, 20 mmol) and K_2CO_3 (3.2 g, 24 mmol) in acetonitrile (45 ml). The reaction mixture was then refluxed at 83 °C for 22 h. When the reaction was complete, the mixture was separated by filtration. The filtrate was evaporated under vacuum by a rotary evaporator to give the crude product. The crude product was washed with acetone two times and dried under vacuum overnight. After that, the

ligand **TETP** was obtained as a white solid. Yield: 66 % (based on bromide reactant). ¹H-NMR (400 MHz, D₂O): δ = 2.58 (m, 6H, H_a), 0.80 (t, 9H, H_b), 5.34 (s, 6H, H_c), 6.44 (d, 6H, H_d), 7.59(d, 6H, H_e). MS (ESI+, MeOH, m/z): calcd for [M + H]⁺, 484.6; found, 484.8. Melting point: 292 °C.

Synthesis of $[Dy(TETP) \cdot (NO_3)_3] \cdot 4H_2O$ (1): A solution of TETP (30 mg, 0.06 mmol) in water (4 ml) was added to a stirred solution of $Dy(NO_3)_3 \cdot 6H_2O$ (18 mg, 0.04 mmol) in acetone (6 ml) at room temperature. The mixture was stirred for 20 min at room temperature. After filtration, slow diffusion of acetone into the filtrate over one week afforded colorless crystals. Yield: 58 % (based on Dy salt). Anal. Calc. (%) for $C_{30}H_{41}DyN_6O_{16}$: C, 39.85; H, 4.57; N, 9.29. Found: C, 39.91; H, 4.36; N, 9.51.



Fig. S1 The measured powder XRD patterns of Dy(III)-**TETP**-MOF and Gd(III)-**TETP**-MOF in comparison to the simulated pattern of single-crystal Dy-MOF (complex 1).



Fig. S2 Solution absorption spectrum (5×10^{-5} M in methanol) of the ligand TETP (left), solid-state absorption spectra of the ligand TETP (middle) and the complex 1 (right).



Fig. S3 Solid-state excitation (left, monitored at 430 nm) and emission spectra (right, excited at different wavelengths) of the ligand **TETP**. T = 298 K, τ = 1.2 and 2.2 ns



Fig. S4 The luminescent lifetime decay curves of complex 1 monitored at 573 nm (left) and 430 nm (right). The observed luminescence decay profile of the 573-nm peak (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$) corresponds to single exponential function with 31 µs, and the 430-nm peak (ILCT) reveals a biexponential decay feature with $\tau = 0.8$ and 3.2 ns.



Fig. S5 Phosphorescence spectrum of Gd(III)-TETP-MOF under excitation at 370 nm; T = 77 K, $\tau = 0.7$ and 6.9 µs.



Fig. S6 Left: Solid-state excitation spectra of complex 1 monitored at 430 nm (red curve) and 573 nm (blue curve) at room temperature. Right: Emission spectrum of complex 1 excited at 265 nm.



Fig. S7 Emission spectra of complex 1 excited at different λ_{ex} at 77 K (left) and, chromaticity coordinates of 1 at different excitations at 77 K (right, $\lambda_{ex} = 290$, 338, 365 and 373 nm; CIE = (0.37, 0.41), (0.27, 0.28), (0.34, 0.37) and (0.20, 0.18), respectively).

O(1)-Dy(1)	2.299(6)	O(2)-Dy(1)#1	2.314(6)	O(3)-Dy(1)#2	2.253(7)
O(4)-Dy(1)	2.498(8)	O(5)-Dy(1)	2.515(7)	O(7)-Dy(1)	2.468(7)
O(8)-Dy(1)	2.530(7)	O(10)-Dy(1)	2.500(7)	O(11)-Dy(1)	2.547(7)
O(3)#3-Dy(1)-O(1)	80.9(3)	O(3)#3-Dy(1)-O(2)#4	81.1(2)	O(1)-Dy(1)-O(2)#4	89.1(2)
O(3)#3-Dy(1)-O(7)	129.9(2)	O(1)-Dy(1)-O(7)	80.0(2)	O(2)#4-Dy(1)-O(7)	143.8(3)
O(3)#3-Dy(1)-O(4)	146.2(3)	O(1)-Dy(1)-O(4)	125.3(3)	O(2)#4-Dy(1)-O(4)	78.7(2)
O(7)-Dy(1)-O(4)	80.0(3)	O(3)#3-Dy(1)-O(10)	91.4(3)	O(1)-Dy(1)-O(10)	141.9(3)
O(2)#4-Dy(1)-O(10)	126.8(2)	O(7)-Dy(1)-O(10)	76.7(3)	O(4)-Dy(1)-O(10)	79.6(3)
O(3)#3-Dy(1)-O(5)	145.1(3)	O(1)-Dy(1)-O(5)	74.7(2)	O(2)#4-Dy(1)-O(5)	73.9(2)
O(7)-Dy(1)-O(5)	70.0(2)	O(4)-Dy(1)-O(5)	50.6(2)	O(10)-Dy(1)-O(5)	123.1(3)
O(3)#3-Dy(1)-O(8)	79.2(3)	O(1)-Dy(1)-O(8)	73.8(2)	O(2)#4-Dy(1)-O(8)	155.6(2)
O(7)-Dy(1)-O(8)	51.0(2)	O(4)-Dy(1)-O(8)	125.3(2)	O(10)-Dy(1)-O(8)	68.1(3)
O(5)-Dy(1)-O(8)	116.3(2)	O(3)#3-Dy(1)-O(11)	74.3(3)	O(1)-Dy(1)-O(11)	153.6(3)
O(2)#4-Dy(1)-O(11)	78.5(2)	O(7)-Dy(1)-O(11)	123.2(2)	O(4)-Dy(1)-O(11)	75.3(3)
O(10)-Dy(1)-O(11)	49.1(2)	O(5)-Dy(1)-O(11)	122.6(2)	O(8)-Dy(1)-O(11)	109.5(3)

Table S1 Selected bond distances (Å) and angles (°) for complex 1.

Symmetry transformations used to generate equivalent atoms: #1, x+1/2, -y+1/2, z; #2, -x+3, -y+1, z+1/2; #3, -x+3, -y+1, z-1/2; #4, x-1/2, -y+1/2, z.

1. "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.

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3. G. Sheldrick, "SHELXL-2013", 2013, Universität Göttingen, Göttingen, Germany.

4. A. L. Spek, , J. Appl. Cryst. 2003, 36, 7-13.