Ameliorated synthetic methodology of crystalline lanthanoid-metalloporphyrin open frameworks based on the multi-topic octacarboxy-porphyrin scaffold; structural, gas sorption and photophysical properties

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Experimental section

**Materials and Methods** All the chemicals were received as reagent grade and used without any further purification. The porphyrin building block Zn-H$_8$OCPP was prepared according to literature procedures.$^{[1]}$ Infrared spectra of solid samples were obtained Bruker Tensor 27 system spectrophotometer in ATR mode. Powder X-ray diffraction patterns were recorded on a Bruker D8-Advance diffractometer using graphite monochromated CuK$_\alpha_1$ (1.5406 Å) and K$_\alpha_2$ (1.54439 Å) radiation. Gas adsorption isotherms of Gd-MPF-1 were performed by using Quantachrome gas adsorption analyzer. Photo physical studies were performed through spin coating of the crystalline LnMPFs in toluene solutions on a glass slide. The experiments were done on Horiba scientific FluorEssence spectrophotometer by placing the LnMPF-1 coated glass slide at 0° to the detector.

**Synthesis of LnMPF-1 (Ln=Gd, Sm, Dy, Eu and Tb).** Zn-H$_8$OCPP (2.5 mg, 0.0025 mmol) and Ln(NO$_3$)$_3$.xH$_2$O (10.0 mg) were dissolved in 500 µl DMF. The mixture was sealed in a screw cap vial and heated at 120°C in a bath reactor. After two hours 325 µL of 1N NaOH was added and sonicated for few minutes to obtain a purple turbid solution which was then heated at same temperature for 7 days to obtain a block shaped crystals of LnMPF-1s along with white powder. The crystals were separated by filtration and washed with DMF, acetone and water several times, air dried for further characterizations For GdMPF-1, Yield : ~15 %. FTIR (cm$^{-1}$): 3367, 2924, 2361, 2084, 1538, 1428, 1369, 995, 775, 712, 418

**Crystal Structure Determinations.** The X-ray measurements (ApexDuo, Bruker-AXS, MoKα radiation) for the analyzed LnMPF-1 compounds [Ln = Gd (1), Sm (2), Dy (3), Eu (4) and Tb (5)] were carried out at ca. 110(2) K on crystals coated with a thin layer of amorphous oil to minimize crystal deterioration, possible structural disorder and related thermal motion effects, and to optimize the precision of the structural results. Compounds 1-5 are isostructural, exhibiting very similar unit-cell dimensions. Full crystallographic analysis was performed on 1-4; crystals of 5 were of very poor quality and were found unsuitable for independent crystal structure determination. Structures 1-4 were solved by direct methods and refined by full-matrix least-squares (SHELXTL-2014 and SHELXL-2014)$^{[2]}$ They were found to
contain severely disordered crystallization solvent (DMF) within the intra-lattice voids, which couldn't be modeled by discrete atoms. Correspondingly, the contribution of the disordered solvent moieties was subtracted from the diffraction pattern by the SQUEEZE procedure and PLATON software.[3] The five-coordinate Zn(H$_2$O)-OCPP entity was found to exhibit twofold disorder, with the Zn(H$_2$O) fragment displaced in a given unit either above or below the porphyrin macrocycle. The solvent accessible voids in all four structures are in the range of 58-59% of the crystal volume. Due to the disordered solvent in such wide voids, as well as translational pseudo-symmetry, the analyzed crystals diffracted poorly, revealing additional minor disorder of the porphyrin component. Some of them revealed also non-merohedral twinning. The crystal data for **1-4** are (excluding the lattice-included DMF solvent):

1. C$_{52}$H$_{30}$Gd$_2$N$_4$Na$_2$O$_2$Zn, Mr = 1472.65, orthorhombic, space group Imma, a = 27.631(2), b = 29.080(3), c = 13.136(1) Å, V = 10555(3) Å$^3$, T = 110 K, Z = 4, μ(MoKα) = 1.519 mm$^{-1}$, ρ(calcd) = 0.93 g·cm$^{-3}$, 15176 reflections measured to θ = 25.10°, of which 4846 were unique (Rint = 0.054) and 3101 with I > 2σ(I). Final R1 = 0.065 (wR2 = 0.184) for the 3101 data above the intensity threshold, and R1 = 0.087 (wR2 = 0.196) for all unique data. CCDC 1422227.

2. C$_{52}$H$_{30}$Sm$_2$N$_4$Na$_2$O$_2$Zn, Mr = 1458.85, orthorhombic, space group Imma, a = 27.108(4), b = 29.418(3), c = 12.972(2) Å, V = 10345(2) Å$^3$, T = 110 K, Z = 4, μ(MoKα) = 1.402 mm$^{-1}$, ρ(calcd) = 0.94 g·cm$^{-3}$, 19423 reflections measured to θ = 25.09°, of which 4794 were unique (Rint = 0.103) and 1740 with I > 2σ(I). Final R1 = 0.074 (wR2 = 0.167) for the 1740 data above the intensity threshold, and R1 = 0.160 (wR2 = 0.179) for all unique data. CCDC 1422228.

3. C$_{52}$H$_{30}$Dy$_2$N$_4$Na$_2$O$_2$Zn, Mr = 1482.16, orthorhombic, space group Imma, a = 27.1337(11), b = 29.2422(14), c = 13.0757(7) Å, V = 10375(5) Å$^3$, T = 110 K, Z = 4, μ(MoKα) = 1.707 mm$^{-1}$, ρ(calcd) = 0.95 g·cm$^{-3}$, 10069 reflections measured to θ = 25.03°, of which 2528 were unique (Rint = 0.031) and 2088 with I > 2σ(I). Final R1 = 0.052 (wR2 = 0.146) for the 2088 data above the intensity threshold, and R1 = 0.060 (wR2 = 0.150) for all unique data. CCDC 1422229.

4. C$_{52}$H$_{30}$Eu$_2$N$_4$Na$_2$O$_2$Zn, Mr = 1466.13, orthorhombic, space group Imma, a = 27.4347(11), b = 29.9058(12), c = 13.1157(7) Å, V = 10401(1) Å$^3$, T = 110 K, Z = 4, μ(MoKα) = 1.472 mm$^{-1}$, ρ(calcd) = 0.93 g·cm$^{-3}$, 18462 reflections measured to θ =
25.05°, of which 4800 were unique (Rint = 0.076) and 3475 with I > 2\sigma(I). Final R1 = 0.104 (wR2 = 0.282) for the 3475 data above the intensity threshold, and R1 = 0.122 (wR2 = 0.290) for all unique data. CCDC 1422230.

**Fig S1.** Projection of 1D zig-zag tubular channels along a, b and c axis (left to right)

**Fig S2.** The illustration of the topological view of \{NaGd(H$_2$O)$_2$\} exhibiting the helical type of chain, which are oriented clock and anti clock wise
**Fig S3.** Thermogravimetric curve of GdMPF-1

**Fig S4.** Powder X-ray patterns of GdMPF-1
**Fig S5a.** Absorbance and emission spectra of Zn-H$_2$OCPP.

**Fig S5b.** Excitation, emission spectra (left) and absorption spectra (right) of SmMPF-1

**Fig S5c.** Excitation, emission spectra (left) and absorption spectra (right) of TbMPF-1
Fig S5d. Excitation and emission spectra GdMPF-1

References

