SUPPLEMENTARY INFORMATION

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_8OCPP 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 CuKα_1 (1.5406 Å) and Kα_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 o° to the detector.

Synthesis of LnMPF-1 (Ln=Gd, Sm, Dy, Eu and **Tb)**. Zn-H_8OCPP (2.5 mg, 0.0025 mmol) and $Ln(NO_3)_3.xH_2O$ (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_2O)-OCPP entity was found to exhibit twofold disorder, with the Zn(H_2O) 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**) $C_{52}H_{30}Gd_2N_4Na_2O_{21}Zn$, 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(MoKa) = 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**) $C_{52}H_{30}Sm_2N_4Na_2O_{21}Zn$, 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(MoKa) = 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**) $C_{52}H_{30}Dy_2N_4Na_2O_{21}Zn$, 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(MoKa) = 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**) $C_{52}H_{30}Eu_2N_4Na_2O_{21}Zn$, 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(MoKa) = 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 > 2σ(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.

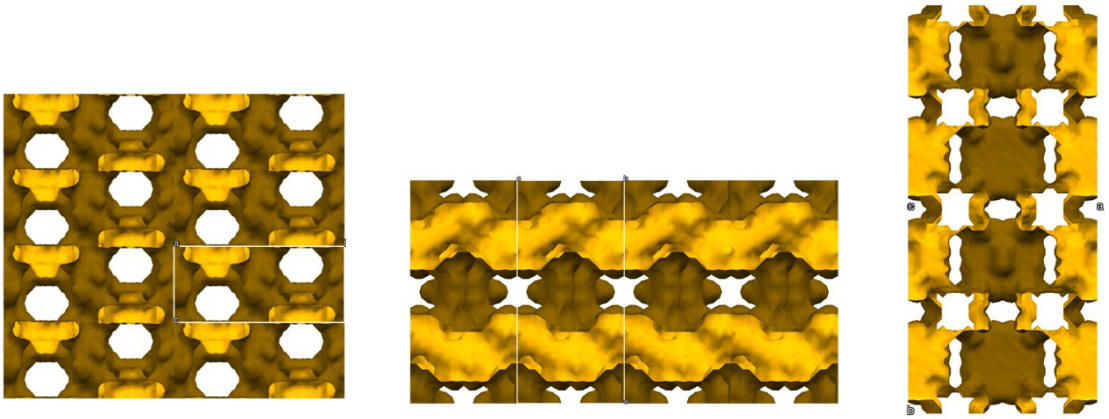

Fig S1. Projection of 1D zig-zag tubular channels along a, b and c axis (left to right)

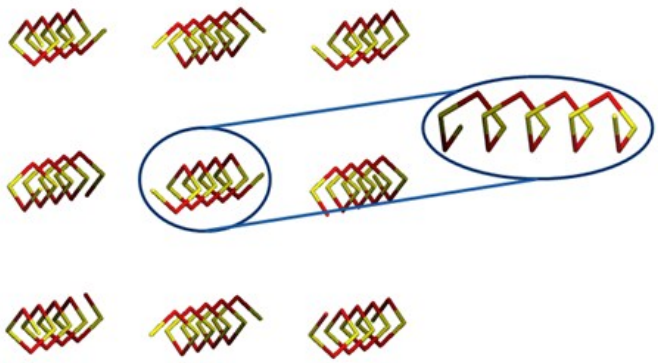

Fig S2. The illustration of the topological view of {$NaGd(H_2O)_2$}exhibiting the helical type of chain, which are oriented clock and anti clock wise

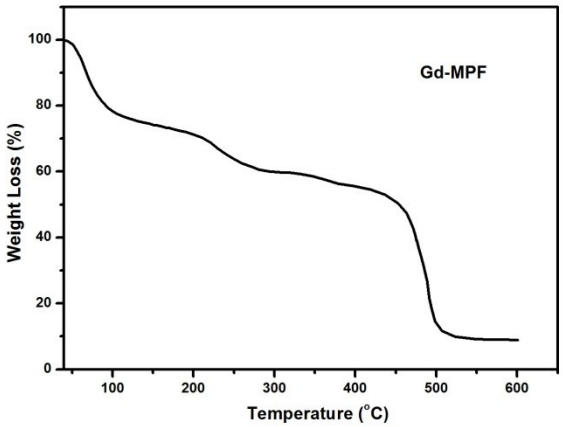

Fig S3. Thermogravimetric curve of GdMPF-1

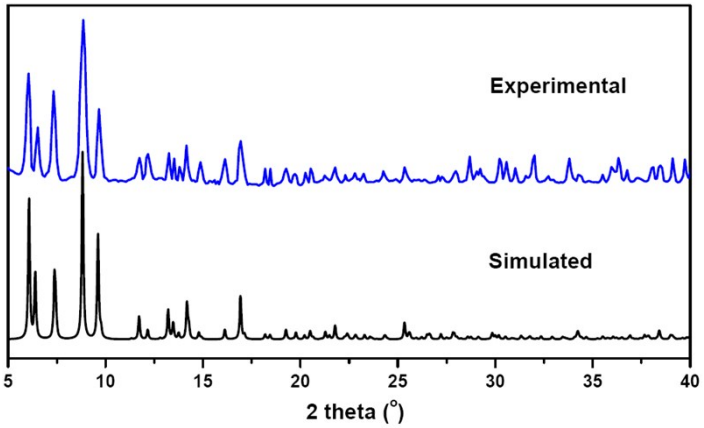

Fig S4. Powder X-ray patterns of GdMPF-**1**

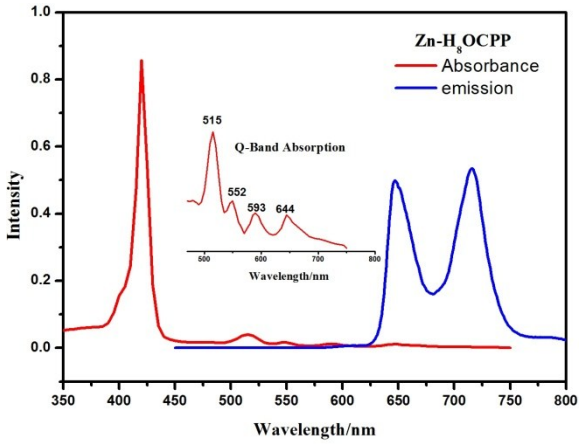

Fig S5a. Absorbance and emission spectra of Zn-H_8OCPP.

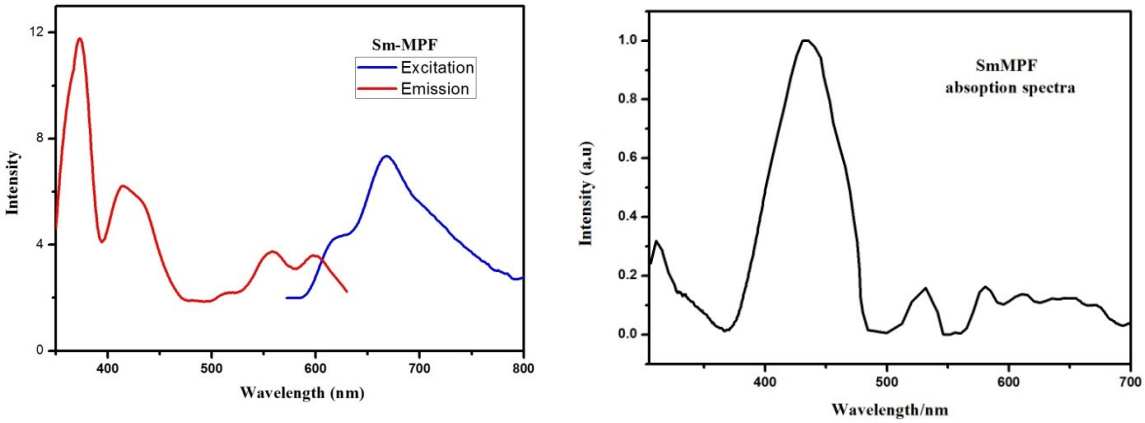

Fig S5b. Excitation, emission spectra (left) and absorption spectra (right) of SmMPF-1

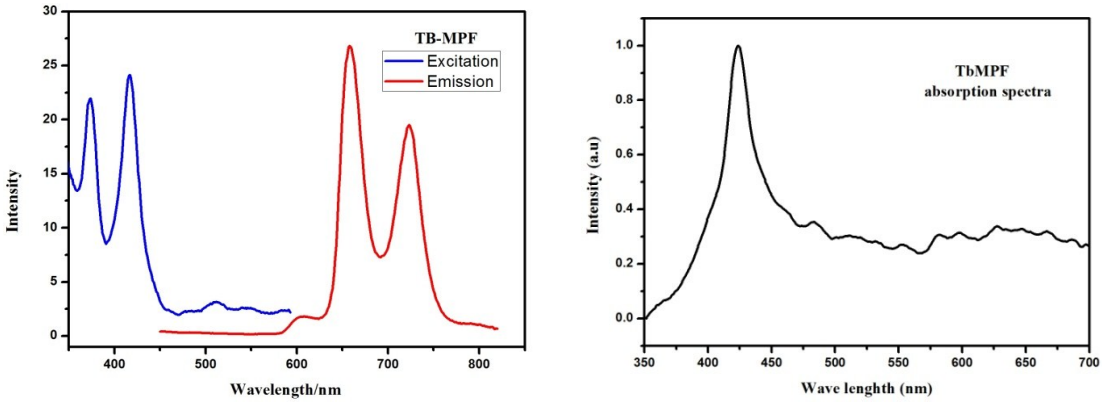

Fig S5c. Excitation, emission spectra (left) and absorption spectra (right) of TbMPF-1

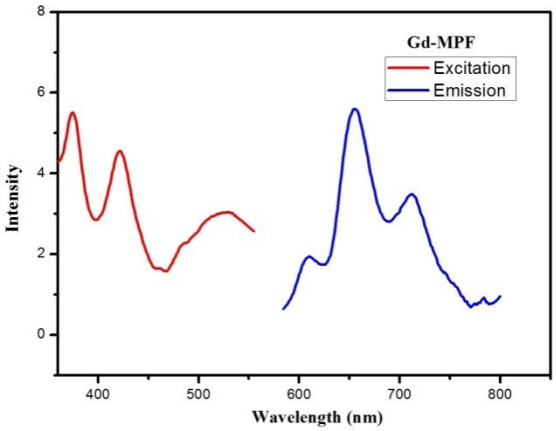

Fig S5d. Excitation and emission spectra GdMPF-1

References

[1] W. Fudickar, J. Zimmermann, L. Ruhlmann, J. Schneider, B. Ro1der, U. Siggel, J.-H. Fuhrhop, *J. Am. Chem. Soc.* **1999**, *121*, 9539-9545.

[2] (a) G. M. Sheldrick, *Acta Cryst.* **2015**, A*71*, 3-8. (b) G. M. Sheldrick, *Acta Cryst.* **2015**, C*71*, 3-8.

[3] A. L. Spek, *Acta Cryst.* **2015**, C*71*, 9-18.