[Supporting Information (SI) to accompany:]

Increasing the Optical Transmittance via Decreasing Crystallite Dimensions—Insights on MOF Luminescence Sensing Applications

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Section S1. General procedures, materials, and instrumentations

Materials.
All materials were used as received without further purification. Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), formic acid, acetone and DMF were purchased from Sigma-Aldrich. Acetic acid was purchased from EMD Millipore. 1,4-Naphthalenedicarboxylic acid (1,4-NDC) was purchased from Alfa Aesar. DEF was purchased from TCI-America. UHP level nitrogen for nitrogen adsorption isotherm was purchased from Matheson Tri-Gas.

Method of Characterization and Instrumentations.
Solvothermal synthesis was carried out in Fisher Isotemp forced air convection oven.

Centrifugation of samples was carried out using Thermo Sorvall ST8 centrifuge. HIGHConic III fixed angle rotor (Cat. # 75005709) were used to hold a maximum of 6 sample tubes at the same time.

For SEM imaging, materials were dispersed in dry ethanol and then dropcast onto Si wafer substrates. They were then imaged in a FEI Helios 660 Nanolab SEM/FIB. Images were recorded in immersion mode with beam deceleration on at 2 keV landing energy with a 0.2 nA probe. For TEM imaging, material was dispersed in dry ethanol, and the dropcast onto Cu grids with a Lacey C film. STEM imaging was performed in a probe-corrected FEI Themis Z operated at 300 kV accelerating voltage.

Powder X-Ray diffraction data were collected on a Rigaku model Smartlab diffractometer using 2theta-omega scans.

Single crystal X-Ray diffraction was performed on an Oxford SuperNOVA Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas AS2 CCD detector. Detail for measurement and refinement can be found Section S3.

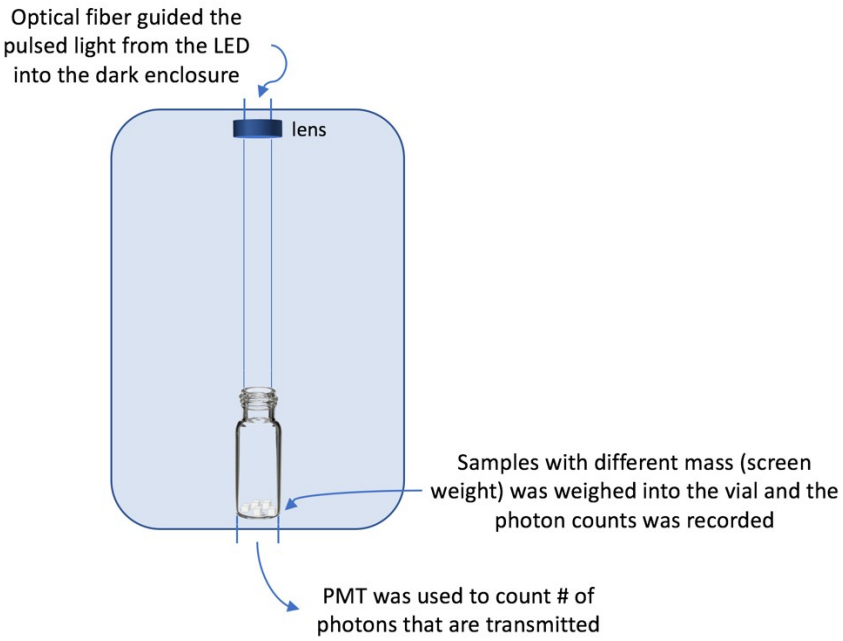
Sample activation and N_2 sorption isotherm measurements were performed on a Micromeritics ASAP 2020 (Micromeritics, Norcross, GA) at 77K. Between 30 and 100 mg of material was used for each measurement. Surface areas were estimated by applying the Brunauer– Emmett–Teller (BET) equation.

Thermogravimetric analyses (TGA) were performed on a TGA/DCS 1 system (Mettler-Toledo AG, Schwerzenbach, Switzerland), which runs on a PC with STAR^e software. Samples were held at 80 °C isothermally for 30 mins, and then heated from 65 to 600 °C at a rate of 5 °C/min under flowing air.

NMR of the digested MOF sample was collected on a Bruker Ascend 500 MHz NMR system with automatic sampler. 32 scans were taken.

Transmission of Zr-1,4-NDC with various sizes were carried out in a homemade setup. Commercially available LED (Everlight, SKU: 12760028) was controlled by a pulse generator to

generate 1 ms pulses of single wavelength green (518 nm) or red light (632 nm). The generated pulses were attenuated and guided by optic fiber (Ocean Optics) into a dark enclosure. The light came in from the top of the enclosure and went through a lens (Ocean Optics) to collimate onto the aperture of the PMT tube (Hamamatsu). The number of photons was counted by a Teledyne LeCroy oscilloscope.



Scheme S1. Scheme for the home-built setup for transmission measurement

Section S2. Synthesis of Zr-1,4-NDC in various sizes (*s,m,n*)

Zr-1,4-NDC (single crystal)

In a 20 cc scintillation vial with PTFE lined cap, $ZrOCl_2 \cdot 8H_2O$ (48 mg, 0.148 mmol), 1,4-NDC (26 mg, 0.12 mmol) were dissolved in a mixture of DEF (8 mL) and formic acid (8 mL) with the aid of sonication. The vial was heated in a convection oven at 135 °C for 2 days or until two thirds of the solvent were evaporated. Then the supernatant was decanted, and the solid was washed with fresh DMF three times over the course of one day. Then the solvent was exchanged to acetone for three times over the course of one day, and the MOF was activated at 120 °C under dynamic vacuum.

Zr-1,4-NDC (microcrystalline powder)

In a 6- dram vial with rubber lined cap, $ZrOCl_2 \cdot 8H_2O$ (72 mg, 0.222 mmol), 1,4-NDC (39 mg, 0.18 mmol) were dissolved in a mixture of DEF (12 mL) and formic acid (2 mL) with the aid of sonication. The uncapped glass vial was placed inside a 45mL PTFE liner with cap, which was sealed inside a 45mL Parr acid digestion vessel and heated in a convection oven at 135 °C for 2 days. The supernatant was decanted, and the solid was washed with fresh DMF three times over

the course of two days and methanol five times over 3 days. The white MOF powder was activated at 115°C under dynamic vacuum for 16 hours.

Zr-1,4-NDC (nanoparticles)
In a 6- dram vial with rubber lined cap, 1,4-NDC (162.5 mg, 0.75 mmol) was dissolved in a mixture of DMF (10 mL) and acetic acid (1.38 mL) using sonication. $ZrOCl_2 \cdot 8H_2O$ (52.5 mg, 0.162 mmol) was then added into this clear solution, and the mixture was sonicated until full dissolution. The reaction mixture was heated in a convection oven at 90 °C for 4.5 hours, and the colloidal solution was subject to centrifugation at 8700 rpm for 7 hours. The supernatant was decanted and the solid was soaked in fresh DMF (50 mL) for 8 hours, and the solvent was exchanged to acetone for two times over 2 days. The MOF was then activated at 120 °C under dynamic vacuum.

Section S3. Details for single crystal measurement

A colorless blocklike crystal of 1 having dimensions 0.163 x 0.131 x 0.085 mm3 was secured to Mitegen micromount using Paratone oil and its single crystal X-ray diffraction data was collected using microfocused Cu Kα1 radiation (1.54184 Å) at 100 K from a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas AS2 CCD detector. A data collection strategy to ensure desired completeness and redundancy was determined via CrysAlisPro [1]. Data processing was done using CrysAlisPro and included a multi-scan absorption correction applied using the SCALE3 ABSPACK scaling algorithm [2]. The structure was solved via intrinsic phasing using SHELXT [3] and refined using SHELXTL [4] in the Olex2 graphical user interface [5]. The space group was unambiguously verified by PLATON [6]. The final structural refinements on samples included anisotropic temperature factors on the zirconium cluster and the carbon atom from the carboxylate group. With the high level of disorder within the naphthalene dicarboxylate linker, peaks in the difference map attributed to atoms from the various components of that disordered linker were identified and had their occupancies fixed to values which authored good thermal parameters and led to a whole number molecular formula upon the application of symmetry. Crystallographic data for the structures in this paper has been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Single crystal X-ray data for compound **1**.

Compound	**1**
CCDC code	
Formula	$C_{144}O_{64}Zr_{12}$
Formula weight	3846.85
Temperature, K	100(1)
Space group	*Fm-3m*
a, Å	20.7859(1)
b, Å	20.7859(1)
c, Å	20.7859(1)
α, deg	90.00

β, deg	90.00
γ, deg	90.00
volume, Å^3	8980.6(1)
Z	2
Density (calculated), mg/m^3	1.423
μ, mm^{-1}	6.147
Scan	ϕ scans
ϑ range for data collection, deg	6.022-66.566
Reflections measured	15608
Independent observed reflns.	460
Independent reflns. [I>2σ]	457
Data/restraints/parameters	460/20/47
R_{int}	0.0264
Final *R* Indices [I>2σ]	R_1 = 0.0658
	*wR*2 = 0.1867
R Indices (all data)	R_1 = 0.0659
	*wR*2 = 0.1867
Goodness-of-fit on F^2	1.125

Table S2. Selected bond distances for **Zr-1,4-NDC**.

Bond	Distance, Å
Zr(1)-O(1)	2.139(4)
Zr(1)-O(2)	2.200(7)
O(2)-C(1A)	1.36(3)
O(2)-C(1B)	1.67(4)
C(1A)-C(2A)	1.46(6)
C(2A)-C(3A)	1.33(2)
C(3A)-C(4A)	1.60(4)
C(4A)-C(5)	1.50(4)
C(1B)-C(2B)	1.86(6)
C(2B)-C(3B)	1.33(2)
C(3B)-C(4B)	1.62(5)
C(5)-C(4B)	1.50(4)
C(5)-C(6)	1.40(5)

Table S3. Selected bond angles for **Zr-1,4-NDC**.

Angle	Deg.
O(1)-Zr(1)-O(2)	142.3(2)
Zr1-O(2)-C(1A)	133.0(17)
Zr1-O(2)-C(1B)	134.0(3)
C(1A)-C(2A)-C(3A)	118.0(3)
C(2A)-C(3A)-C(4A)	129.0(4)
C(3A)-C(4A)-C(5)	150.0(4)
C(4A)-C(5)-C(6)	128.0(3)
C(1B)-C(2B)-C(3B)	120.0(3)
C(2B)-C(3B)-C(4B)	134.0(5)
C(3B)-C(4B)-C(5)	137.0(4)
C(4B)-C(5)-C(6)	127.0(4)

Section S4. TGA traces for Zr-1,4-NDC in various sizes

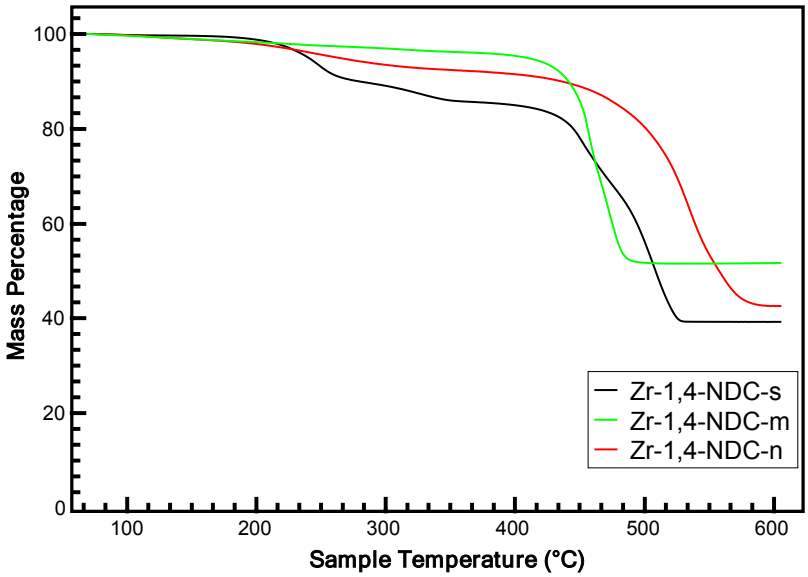


Figure S1. TGA traces for Zr-1,4-NDC-(s,m,n).

Section S5. NMR spectrum for digested Zr-1,4-NDC-s

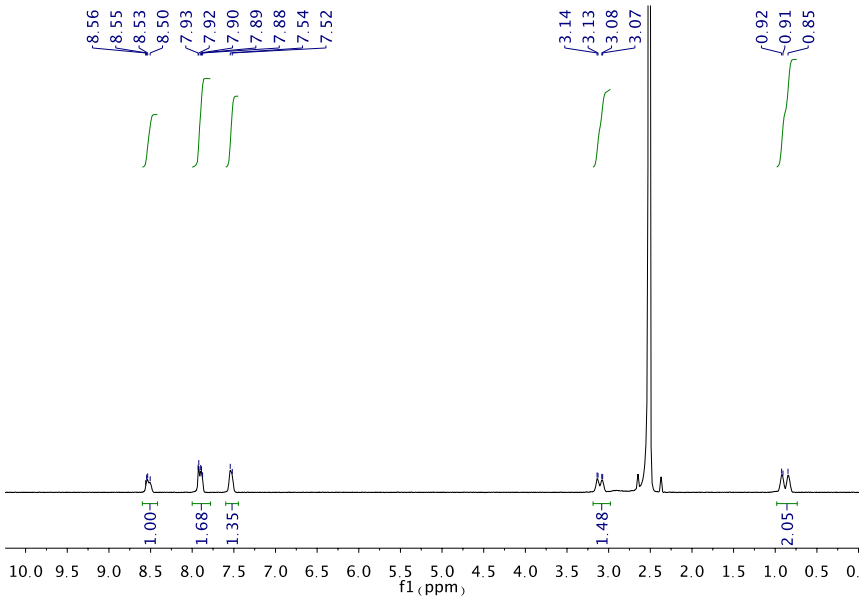


Figure S2. NMR spectrum for digested Zr-1,4-NDC-s. The ethyl peaks for the DEF are those at ~0.91 ppm and 3.13 ppm

Section S6. Light transmission measured by green LED light (518 nm)

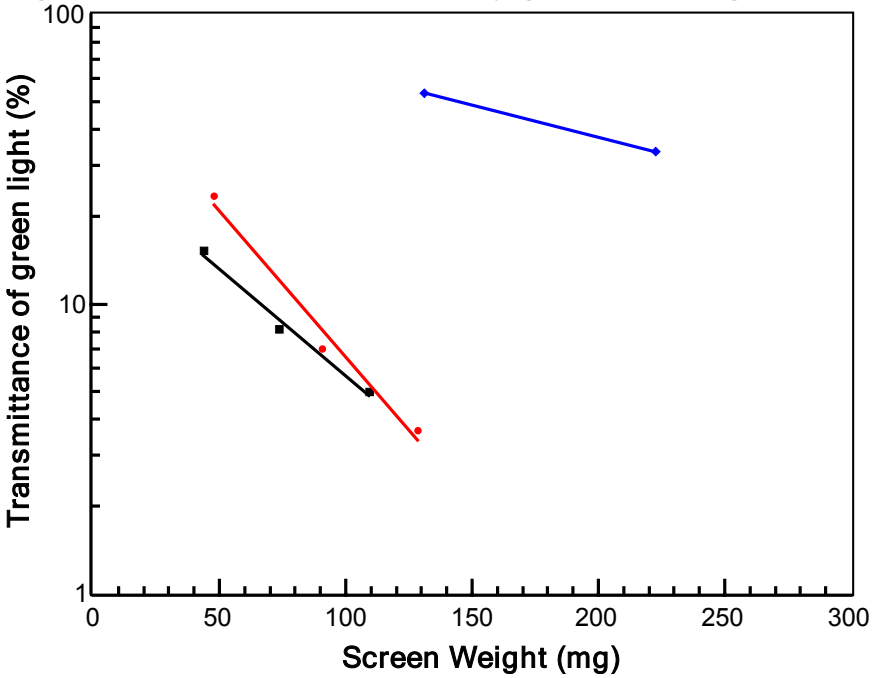


Figure S3. Light transmission measured by green LED light (518 nm). Blue: Zr-1,4-NDC-n, Black: Zr-1,4-NDC-m, Red: Zr-1,4-NDC-s.

Section S7. Luminescence spectrum for Zr-1,4-NDC

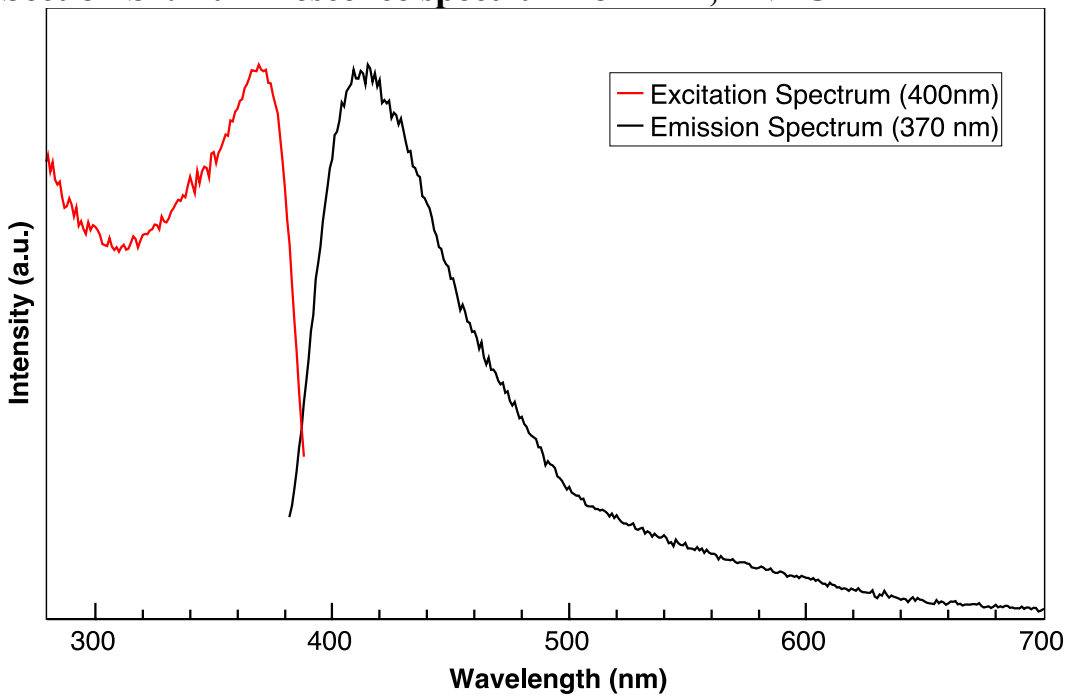


Figure S4. Excitation (red) and emission (black) spectrum for Zr-1,4-NDC. Excitation and fixed emission wavelength are specified in the parenthesis in legend.

Section S8. References

1) CrysAlisPro, Rigaku Oxford Diffraction, version 171.39.46, **2018**.

2) SCALE3 ABSPACK – A Rigaku Oxford Diffraction program for Absorption Corrections, Rigaku Oxford Diffraction, **2017**.
3) Sheldrick, G.M. (**2015**). Acta Cryst. A71, 3-8.

4) Sheldrick, G.M. (**2015**). Acta Cryst. C71, 3-8.

5) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (**2009**), J. Appl. Cryst. 42, 339-341.

6) A.L. Spek, Acta Cryst. **2009**, D65, 148-155.