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Supporting Information

The Effect of Cluster Size on the Optical Band Gap Energy of Znbased Metal-Organic Frameworks

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Experimental Section

Materials. All chemicals were of reagent-grade quality obtained from Sigma-Aldrich and used as received without further purification. The FT-IR spectrum was recorded from KBr pellets in the range of 4000-400 cm⁻¹ on a SHIMADZU FT-IR spectrometer. The TGA was performed on SDT Q600 (Shimadzu) analyser in flowing nitrogen with a heating rate of 10 $^{\circ}$ C per minute. Powder X-ray diffraction data were collected using an X'pert PRO (PANanalytics) powder diffractometer equipped with Cu K α radiation (1.540598 Å).

Synthesis of [Zn(SDB)(DMF)]. DMF, 1: $Zn(NO_3)_2$.6H₂O (0.5 mmol) and 4, 4'sulfonyldibenzoic acid (SDB) (0.5 mmol) were dissolved in 10 mL of dimethyformamide (DMF), in a 25 mL glass vial. The glass vial was placed in an oven and heated to 130 °C for 72 h and then cooled to room temperature. Colourless crystals were formed. The crystals were then washed several times with DMF and the suitable crystal was isolated for single crystal X-ray diffraction. Yield of the product was 80% based Zn metal.

Synthesis of $[Zn_3(SDB)_3(DMF)_3]$. DMF, 2: $Zn(NO_3)_2$. $6H_2O$ (0.5 mmol) and 4, 4'sulfonyldibenzoic acid (SDB) (0.5 mmol) were dissolved in a mixture of 10 mL of dimethyformamide (DMF), 2 mL methanol and 2 mL ethanol in a 25 mL glass vial. The glass vial was placed in an oven and heated to 130 °C for 72 h and then cooled to room temperature. Colourless crystals were formed. The crystals were then washed several times with DMF and the suitable crystal was isolated for single crystal X-ray diffraction. Yield of the product was 70% based Zn metal.

Synthesis of $[Zn_3(OH)_2(SDB)_2]$. DMF, 3: $Zn(NO_3)_2$. $6H_2O$ (0.5 mmol) and 4, 4'-sulfonyldibenzoic acid (SDB) (0.5 mmol) were dissolved in a mixture of 10 mL of dimethyformamide (DMF), 2 mL ethanol and 0.25 mL water in a 25 mL glass vial. The glass

vial was placed in an oven and heated to 130 °C for 72 h and then cooled to room temperature. Colourless crystals were formed. The crystals were then washed several times with DMF and the suitable crystal was isolated for single crystal X-ray diffraction. Yield of the product was 80% based Zn metal.

Single Crystal X-ray Diffraction. For single crystal XRD measurement, a suitable crystal for all the compounds were carefully selected under a polarizing microscope and glued to a thin glass fiber. The single crystal diffraction data were collected on a Bruker AXS Smart Apex CCD diffractometer at 298 K. The X-ray generator was operated at 50 kV and 35 mA using MoK_{α} (λ = 0.71073 Å) radiation. Data were collected with ω scan width of 0.3°. A total of 606 frames were collected in three different settings of φ (0°, 90°, 180°) keeping the sample to-detector distance fixed at 6.03 cm and the detector position (2 θ) fixed at -25°.

The data were reduced using SAINTPLUS¹ and an empirical absorption correction was applied using the SADABS program.² The crystal structure was determined by direct methods using SHELXS97 and refined using SHELXL97 present in the SHELXTL V6.14³ package. All hydrogen atoms were placed in calculated positions during the final step of the refinement process. For the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined using the riding mode. The last cycles of the refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against F² was carried out using the WINGX⁴ package of programs. The crystallographic parameters for all the compounds are provided in table S1. CCDC 1052870-1052872 contains the crystallographic data for **1** – **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc. cam.ac.uk/data_request/cif

References:

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Initial Characterizations

Initial characterizations were carried out by elemental analysis, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and IR spectroscopic studies. Elemental analysis calculated (%) for compound 1: calculated (%) C, 46.57; H, 4.30; N, 5.43 found: C, 46.52; H, 4.28; N, 5.40. For compound 2: calculated (%) C, 46.28; H, 3.74; N, 4.00 found: C, 46.25; H, 3.75; N, 4.01. For compound 3: calculated (%) C, 41.46; H, 3.27; N, 2.84 found: C, 41.44; H, 3.24; N, 2.82.

Optical band-gap measurements

The variations in the architectures and compositions of the assemblies lead to different electronic, optical, and other properties. To demonstrate this, we measured the optical band gaps of compounds 1 - 3, free ligand and Na-salt of ligand using diffuse reflectance spectroscopy, and the Kubelka-Munk model. The optical absorption spectra of all MOF samples, free ligand and Na-salt of ligand were collected on a Shimadzu UV/Vis/NIR spectrophotometer. The room temperature diffuse reflectance spectra was measured using BaSO₄ as a reference material and converted to a Kubelka–Munk function, from which the band gap of the compound was estimated. This two-flux model, which considers only diffuse light, is used to determine the absorption coefficients from a surface that both scatters and absorbs incident radiation. For a crystalline solid with a band gap (E_{bg}), the frequency dependence (v) of the absorption coefficient (v) can be approximated as

$$\kappa(v) = \frac{B_T (hv - E_{bg})^n}{hv}$$

where B_T is a constant derived from the square of the averaged dipolar momentum matrix element and n is equal to 0.5 and 2 for direct and indirect band gap transitions, respectively. The absorption coefficient (κ) can be measured from the reflectance (R) and expressed as $\kappa = (1 - R)^2/(2R)$. Using the above equation, the band gap of a material can be obtained by extrapolating to zero with the linear fit to a plot of (khy)^{1/n} vs hy.

Theoretical Methods

First principles electronic structure studies within a gradient-corrected density functional framework were carried out to understand the experimental findings on the band gaps. Two kinds of theoretical studies were performed. Electronic structure calculations with the PBE exchange-correlation functional¹ were performed on periodic solids using the experimentally determined crystal structures to understand the origins of changes in the band gap energy. These calculations were performed using the Vienna Ab-Initio Simulation Package (VASP).² The projector augmented wave (PAW) pseudopotentials were used to describe the electron-ion interaction.³ The kinetic energy cut-off of 400 eV was found to give converged results and was used for the plane wave basis. The geometries in these studies used the experimentally determined crystal structures. Secondly, gradient-corrected calculations using the PBE functional³¹ were performed on free clusters to understand the nature of bonding, using the Amsterdam Density Functional Package (ADF).⁴ Relativistic effects were taken in account using the Zeroth Order Regular Approximation, and the TZ2P basis set was used.⁵

References

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Parameters	Compound 1	Compound 2	Compound 3
Empirical formula	$C_{18.50}H_{15}N_{1.50}O_{7.50}SZn$	$C_{53}H_{38}N_2O_{20}S_3Zn_3$	$C_{15.50}H_9N_{0.50}O_{7.50}SZn_{1.50}$
Formula weight	475.75	1315.14	452.35
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	C 2/c (No.15)	P $2_1/n$ (No. 16)	$P 2_1/n$ (No. 16)
a (Å)	22.2749	16.3303	13.9367
b (Å)	12.7253	20.6847	6.1040
c (Å)	17.7334	16.9801	19.7129
α (⁰)	90	90	90
β(⁰)	126.3350	98.4720	93.616
γ (⁰)	90	90	90
Volume(Å ³)	4049.3	5673.1	1673.63
Ζ	8	4	4
Calculated density (g/cm ³)	1.561	1.540	1.795
θ range (⁰)	2.852 to 28.275	1.562 to 24.712	1.739 to 28.381
Absorption coefficient (mm ⁻¹)	1.361	1.445	2.333
Reflections collected	17676	43897	15867
Unique reflections	4903	9670	4173
Goodness-of-fit	1.052	1.039	1.085
Number of parameters	277	729	235
Final R indices [I>2sigma(I)]	$R_1 = 0.0330, wR_2 = 0.0835$	$R_1 = 0.0639, wR_2 = 0.1734$	$R_1 = 0.0356, wR_2 = 0.0948$
R indices (all data)	R1 = 0.0508, wR2 = 0.0913	R1 = 0.1173, wR2 = 0.2129	R1 = 0.0668, wR2 = 0.1210

Table S1. Crystallographic parameters for compounds 1, 2 and 3 respectively^[a].

^[a] $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$; wR₂ = {[$w(F_0^2 - F_c^2)^2$]/[$w(F_0^2)^2$]}^{1/2}; $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$; $P = [max(F_0^2, 0) + 2(F_c)^2]/3$, where a = 0.0431 and b = 3.8227 for 1, a = 0.1273 and b = 2.4768 for 2 and a = 0.0000 and b = 0.0667 for 3, respectively.

Moiety	Bond lengths (Å)
Zn(1)-O(1)	1.9857 (16)
Zn(1)-O(2)	2.0207 (17)
Zn(1)-O(3)	2.0207 (17)
Zn(1)-O(4)	2.0420 (16)
Zn(1)-O(5)	2.0894 (16)

Table S2. Selected bond length for compound 1.

Moiety	Bond lengths (Å)
Zn(1)-O(2)	2.025 (5)
Zn(1)-O(6)	2.046 (7)
Zn(1)-O(5)	2.053 (4)
Zn(1)-O(1)	2.053 (5)
Zn(1)-O(4)	2.087 (5)
Zn(1)-O(3)	2.262 (7)
Zn(2)-O(8)	1.941 (5)
Zn(2)-O(7)	1.956 (5)
Zn(2)-O(13)	1.988 (5)
Zn(2)-O(9)	2.045 (6)
Zn(2)-O(3)	2.443 (7)
Zn(3)-O(11)	1.921 (5)
Zn(3)-O(10)	1.923 (5)
Zn(3)-O(12)	1.930 (6)
Zn(3)-O(14)	2.001 (5)

Table S3. Selected bond length for compound **2**.

Table S4. Selected bond length for compound **3**.

Moiety	Bond lengths (Å)
Zn(1)-O(1)	1.9027
Zn(1)-O(2)	1.9158
Zn(1)-O(3)	1.9796
Zn(1)-O(3)#1	2.0032
Zn(2)-O(3)	2.0384
Zn(2)-O(3)#2	2.0385
Zn(2)-O(4)#2	2.0795
Zn(2)-O(4)	2.0796
Zn(1)-O(5)#1	2.1835
Zn(1)-O(5)#3	2.1835

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



Fig. S1 The acid connectivity in compound 1.



Fig. S2 The acid connectivity in compound **2** (a) acid-1, (b) acid-2 and (c) acid-3, respectively.



Fig. S3. The acid connectivity in compound **3**.



Fig. S4. The simulated and experimental powder X-ray pattern of compound 1.



S5. The simulated and experimental powder X-ray pattern of compound 2.



Fig. S6. The simulated and experimental powder X-ray pattern of compound **3**.



Fig. S7. Thermogravimetric plot of compound 1.



Fig. S8. Thermogravimetric plot of compound **2**.



Fig. S9. Thermogravimetric plot of compound **3**.



Fig. S10. The characteristic IR peaks for compounds 1-3.



Fig. S11. Cluster model of a) 1, b) 2, and c) 3.