

Supporting Information

Carboxyl Position Directed Structure Diversity in Zirconium-Tricarboxylate Frameworks

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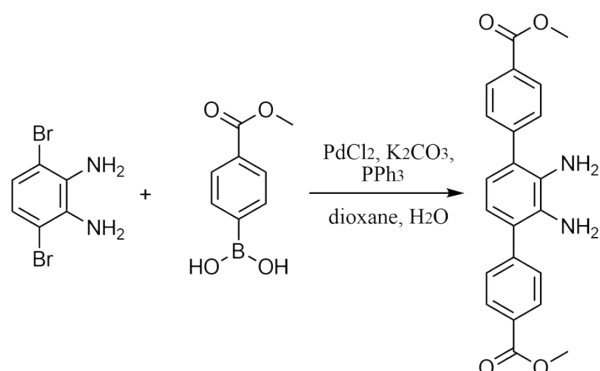
Chemicals

3,6-dibromobenzene-1,2-diamine was purchased from Jilin Chinese Academy of Science-Yanshen Technology Co., Ltd. (4-(methoxycarbonyl)phenyl)boronic acid, methyl 5-formylthiophene-2-carboxylate, methyl 5-formylthiophene-3-carboxylate and ethyl 2-formylthiophene-3-carboxylate were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All the other chemicals were obtained from the chemical supplies and used without further purification.

Characterization

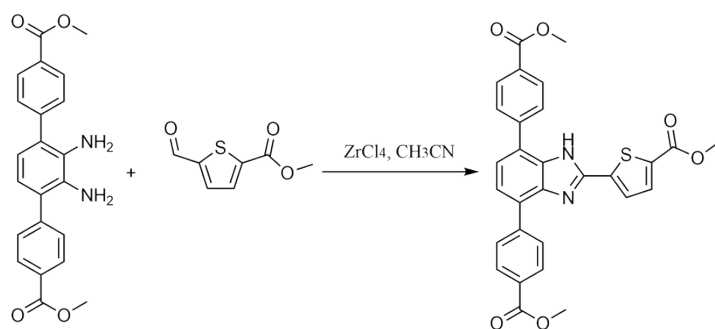
Nuclear magnetic resonance (NMR) data was collected using 400 MHz JEOL JNM-ECZ400S. Single crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer. Powder X-ray diffraction (PXRD) patterns were measured using Bruker D8 Advance X-ray diffractometer with Cu K α radiation. Scanning electron micrographs (SEM) images were taken using a JEOL JSM-IT800 (SHL). UV-vis and photoluminescent spectra were measured on Shimadzu UV-3600 spectrophotometer and FLS1000 spectrofluorometer (Edinburgh Instruments), respectively. TGA data was collected using TGA 550 (TA Instruments) analyzer and the samples were heated from room temperature to 600°C at a ramp rate of 10°C / min.

Synthesis of dimethyl 2',3'-diamino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate



3,6-dibromobenzene-1,2-diamine (10.0 mmol, 2.65 g) (4-(methoxycarbonyl)phenyl)boronic acid (25.0 mmol, 4.49 g), PdCl₂ (0.8 mmol, 0.14 g), PPh₃ (1.60 mmol, 0.42 g) and K₂CO₃ (32.0 mmol, 4.40 g) were added into one 250 mL flask containing 120 mL dioxane and 30 mL water. The mixture was degassed four times and stirred at 105 °C for 12 hours. After cooling down to room temperature, the organic solvent was removed under reduced pressure. The crude product was purified by a flash silica gel column chromatography to offer dimethyl 2',3'-diamino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate as a light yellow solid (3.35 g, 89.2%). ¹H NMR (400 MHz, CDCl₃) δ ppm 8.77-8.44 (4H), 8.20-7.88 (4H), 7.72 (2H), 4.12 (6H).

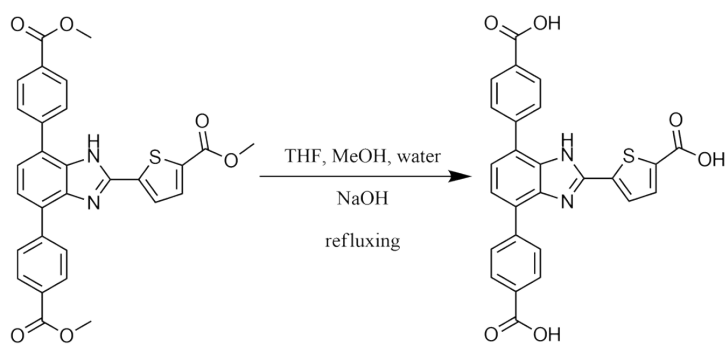
Synthesis of dimethyl 4,4'-(2-(5-(methoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate



Dimethyl 2',3'-diamino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (2.60 mmol, 0.98 g), methyl 5-formylthiophene-2-carboxylate (2.86 mmol, 0.49 g), ZrCl₄ (0.52 mmol, 0.12 g) were added into a flask containing 50 mL CH₃CN. The mixture was stirred at 50 °C for 24 h under N₂ atmosphere. A white precipitate was gradually formed with increased reaction time. After

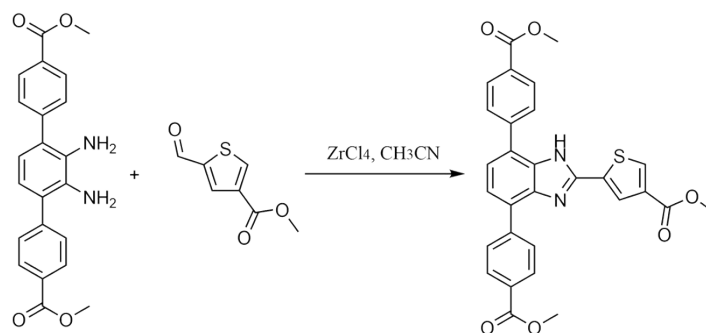
cooling down to room temperature, the precipitate was filtered and washed using CH₃CN to give dimethyl 4,4'-(2-(5-(methoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate as a white solid (1.18 g, 86.6%), which was directly used for next step without further purification.

Synthesis of 4,4'-(2-(5-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid (H₃5CIB)



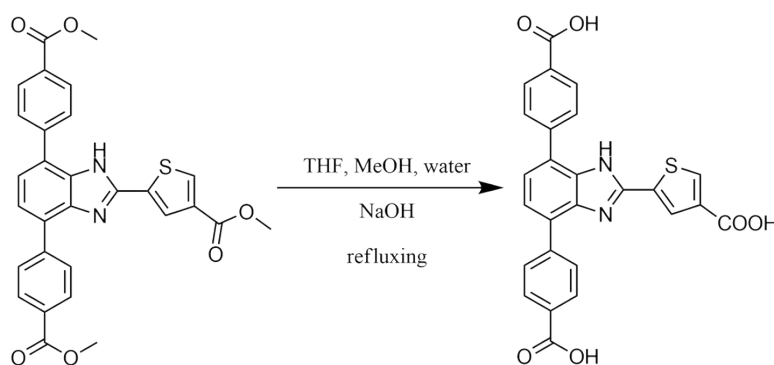
Dimethyl 4,4'-(2-(5-(methoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate (2.0 mmol, 1.05 g) was added to a solution containing 25 mL CH₃OH, 50 mL THF and 50 mL water with 2 g NaOH. The mixture was heated to reflux at 85 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure. Then resulted aqueous was neutralized using 2 M HCl to obtain the precipitate, which was filtered to offer the final product 4,4'-(2-(5-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid as a white solid (0.85, 87.8%). ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 13.08 (3H), 8.25 (2H), 8.14-8.03 (5H), 7.81 (2H), 7.75 (1H), 7.60 (1H), 7.38 (1H).

Synthesis of dimethyl 4,4'-(2-(4-(methoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate



Dimethyl 2',3'-diamino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (2.60 mmol, 0.98 g), methyl 5-formylthiophene-3-carboxylate (2.86 mmol, 0.49 g), $ZrCl_4$ (0.52 mmol, 0.12 g) were added into a flask containing 50 mL CH_3CN . The mixture was stirred at 50 °C for 24 h under N_2 atmosphere. A white precipitate was gradually formed with increased reaction time. After cooling down to room temperature, the precipitate was filtered and washed using CH_3CN to give dimethyl 4,4'-(2-(4-(methoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate as a white solid (1.23 g, 90.1%), which was directly used for next step without further purification.

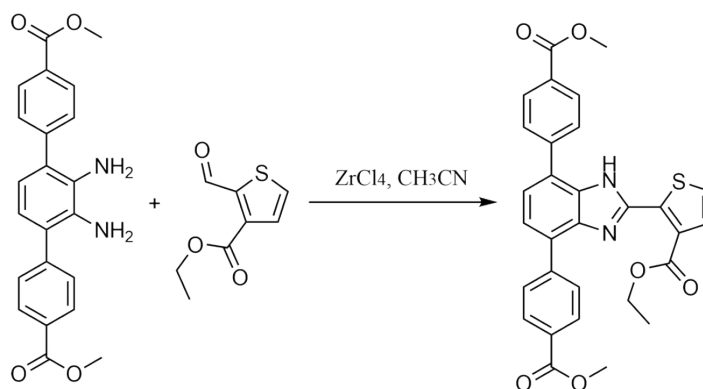
Synthesis of 4,4'-(2-(4-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid (H_34CIB)



Dimethyl 4,4'-(2-(4-(methoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate (2.6 mmol, 1.37 g) was added to a solution containing 25 mL CH_3OH , 50 mL THF and 50 mL water with 2.5 g NaOH. The mixture was heated to reflux at 85 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced

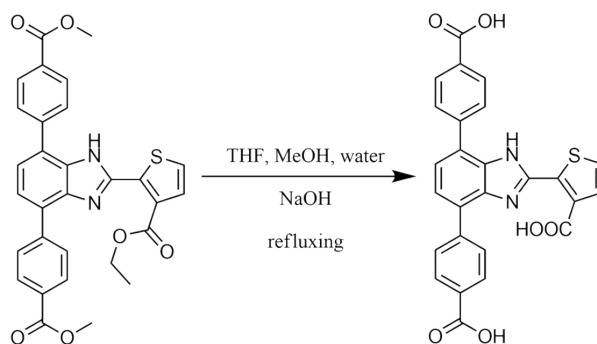
pressure. Then resulted aqueous was neutralized using 2 M HCl to obtain the precipitate, which was filtered to offer the final product 4,4'-(2-(4-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid as a white solid (1.17 g, 92.8%). ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 13.02 (3H), 8.49 (1H), 8.37 (1H), 8.08 (8H), 7.50 (2H).

Synthesis of dimethyl 4,4'-(2-(3-(ethoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate



Dimethyl 2',3'-diamino-[1,1':4,1''-terphenyl]-4,4''-dicarboxylate (2.60 mmol, 0.98 g), ethyl 2-formylthiophene-3-carboxylate (2.86 mmol, 0.53 g), ZrCl₄ (0.52 mmol, 0.12 g) were added into a flask containing 50 mL CH₃CN. The mixture was stirred at 50 °C for 24 h under N₂ atmosphere. A light-brown precipitate was gradually formed with increased reaction time. After cooling down to room temperature, the precipitate was filtered and washed using CH₃CN to give dimethyl 4,4'-(2-(3-(ethoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate as a light-brown solid (1.12 g, 78.0%), which was directly used for next step without further purification.

Synthesis of 4,4'-(2-(3-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid (H₃3CIB)



Dimethyl 4,4'-(2-(3-(ethoxycarbonyl)thiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoate (2.0 mmol, 1.08 g) was added to a solution containing 15 mL CH₃OH, 30 mL THF and 50 mL water with 2.0 g NaOH. The mixture was heated to reflux at 85 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure. Then resulted aqueous was neutralized using 2 M HCl to obtain the precipitate, which was filtered to offer the final product 4,4'-(2-(3-carboxythiophen-2-yl)-1H-benzo[d]imidazole-4,7-diyl)dibenzoic acid as a yellow solid (0.91, 94.0%). ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 8.07 (4H), 7.99 (2H), 7.76 (1H), 7.62 (2H), 7.56 (1H), 7.53 (2H).

Synthesis of HIAM-4033

ZrCl₄ (23.3 mg), H₃5CIB (10 mg) and formic acid (0.4 ml) were added into a 5 mL vial containing 3 mL DMF. After sonicated for 5 minutes, the vial was put into a preheated oven at 120°C for 3 days. After cooling down to room temperature, the colorless single crystals were obtained, which was washed using DMF for several times until no fluorescent signal was detected from the supernatant (yield: 90.1%).

Synthesis of HIAM-4034

ZrCl₄ (23.3 mg), H₃4CIB (10 mg) and formic acid (0.5 ml) were added into a 5 mL vial containing 3 mL DMF. After sonicated for 5 minutes, the vial was put into a preheated oven at 120°C for 3 days. After cooling down to room temperature, the colorless single crystals were obtained, which was washed using DMF for several times until no fluorescent signal was detected from the supernatant (yield: 82.2%).

Synthesis of HIAM-4035

ZrCl₄ (23.3 mg), H₃3CIB (10 mg) and trifluoroacetic acid (40 μL) were added into a 5 mL vial containing 2 mL DEF. After sonicated for 5 minutes, the vial was put into a preheated oven at 120°C for 3 days. After cooling down to room temperature, the colorless single crystals were obtained, which was washed using DMF for several times until no fluorescent signal was detected from the supernatant (yield: 35.4%).

Synthesis of nanosized HIAM-4033

50 mg ZrOCl₂·8H₂O, 10 mg H₃5CIB, 0.3 mL formic acid and 3 mL DMF were added in a 5 mL vial. The mixture was sonicated for several minutes and then put into a preheated oven at 90 °C for 24 h. After cooling down to room temperature, the white product was isolated by

centrifugation at 12000 rpm for 10 minutes, which was further washed with DMF for three times.

Single-crystal X-ray diffraction analyses

Single crystals of HIAM-4033 and HIAM-4034 were mounted on MicroMesh (MiTeGen) with paraton oil. The data were collected on a ' Bruker D8 VENTURE Metaljet PHOTON II ' diffractometer equipped with gallium micro-focus metaljet X-ray sources ($\lambda = 1.34139 \text{ \AA}$). The crystals kept at the 193 K during data collection. Using Olex2¹, the structures were solved with the ShelXT² structure solution program using Intrinsic Phasing and refined with the ShelXL³ refinement package using Least Squares minimization. In the structure of HIAM-4033, a 5CIB ligand is found to be disordered over two sets of sites with occupancy of each part is 0.5. Furtherly, six Zr^{4+} ions form an octahedron with the 8 faces each capped by six $\mu_3\text{-O}$ groups and two $\mu_3\text{-OH}$ groups. Ten edges of the octahedron are bridged by two formate groups and ten carboxylate groups from 5CIB ligands with two formate groups and two carboxylate groups sharing the same sites. The remaining coordination sites of Zr^{4+} are completed by H_2O molecules. In the structure of HIAM-4034, a 4CIB ligand and a dimethylamine cation are found to be disordered over two sets of sites with occupancy of each part is 0.5. Furtherly, six Zr^{4+} ions form an octahedron with the 8 faces each capped by $\mu_3\text{-O}$ groups and $\mu_3\text{-OH}$ groups. Eight edges of the octahedron are bridged by two formate groups and six bidentate carboxylate groups from 4CIB ligands. The remaining coordination sites of Zr^{4+} are completed by H_2O molecules and monodentate carboxylate groups from 4CIB ligands. In the two structures, restraints (DFIX, DANG, SADI, FLAT ISOR and SIMU) were used to refine the 4CIB ligand to make the ADP values of those atoms more reasonable. The hydrogen atoms on the aromatic rings were located

at geometrically calculated positions and refined by riding. The free solvent molecules are highly disordered in MOFs, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these solvent molecules were removed using the Solvent Mask routine of Olex2, structures were then refined again using the data generated. The refinement results are summarized in Table S1 and S2. Crystallographic data for the crystal structures in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-2269047 and CCDC-2269048. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

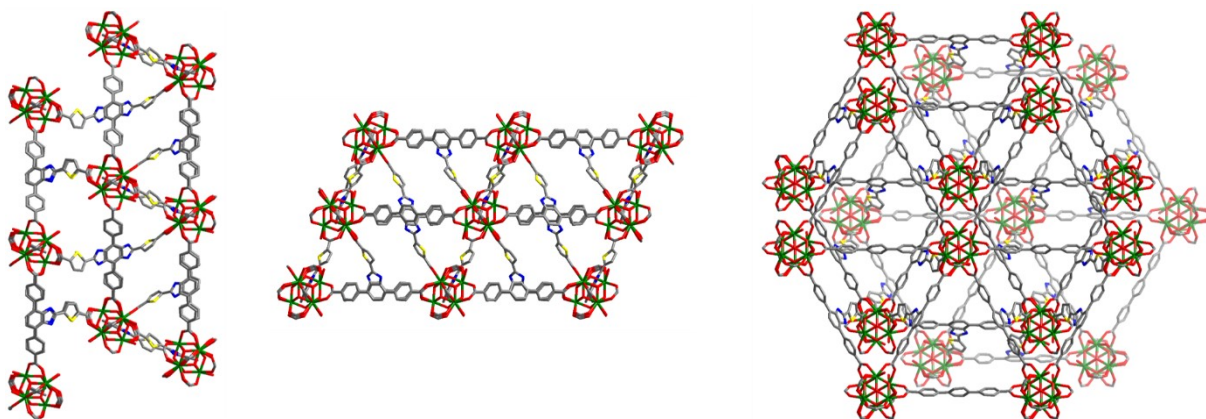


Figure S1. The single crystal structure of HIAM-4033 viewed along *a* axis (left), *b* axis (middle) and *c* axis (right).

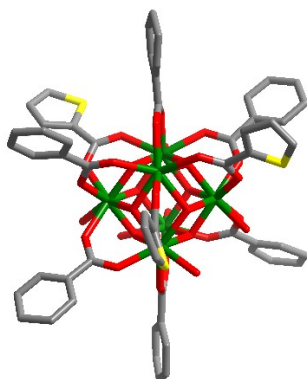


Figure S2. The connection mode Zr₆ cluster in HIAM-4033.

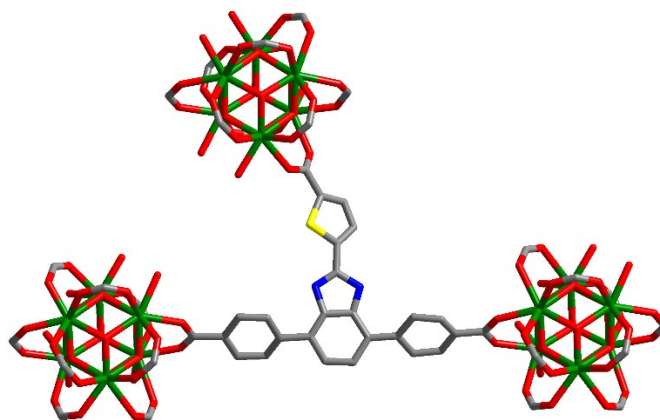


Figure S3. The coordinating modes of carboxylate group in HIAM-4033.

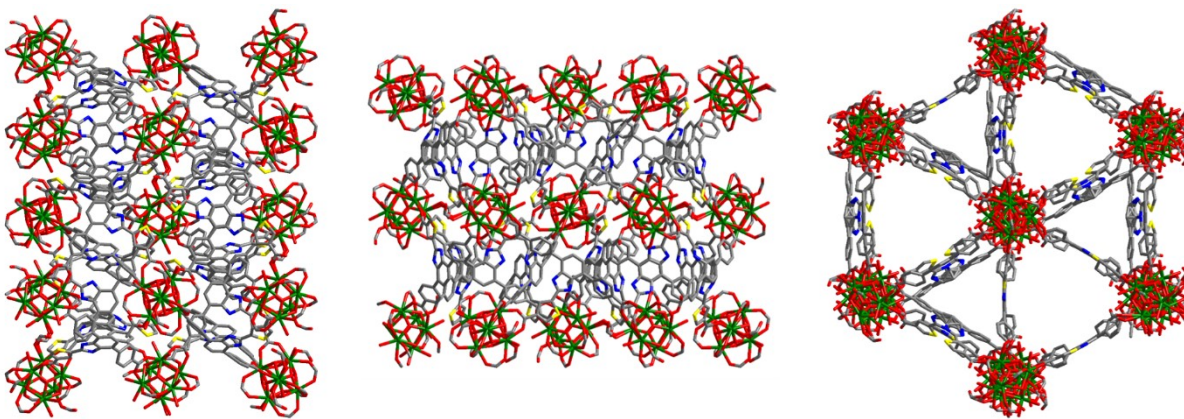


Figure S4. The single crystal structure of HIAM-4034 viewed along *a* axis (left), *b* axis (middle) and *c* axis (right).

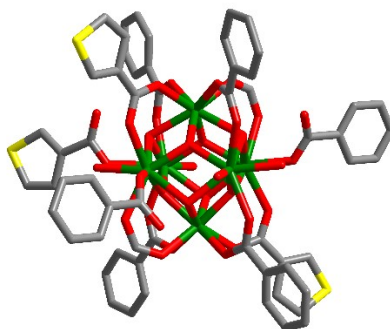


Figure S5. The connection model of organic linkers and Zr_6 cluster in HIAM-4034.

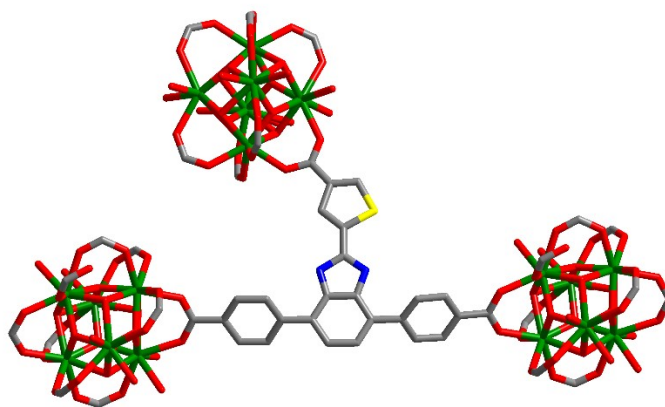


Figure S6. The coordinating modes of carboxylate group in HIAM-4034.

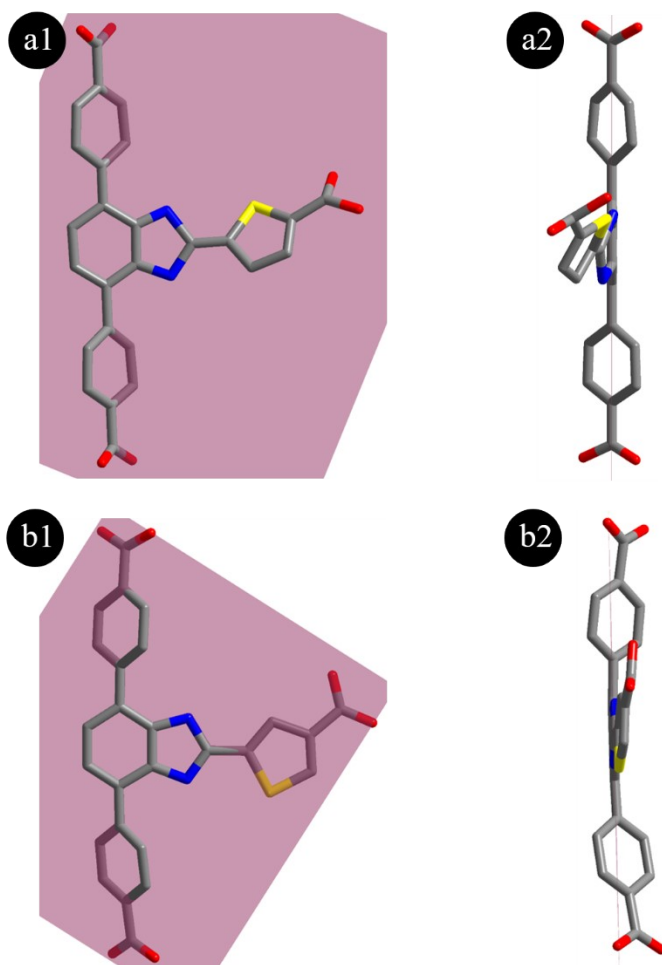


Figure S7. The 5CIB conformations in HIAM-4033 (a1 and a2) and 4CIB conformations in HIAM-4034 (b1 and b2).

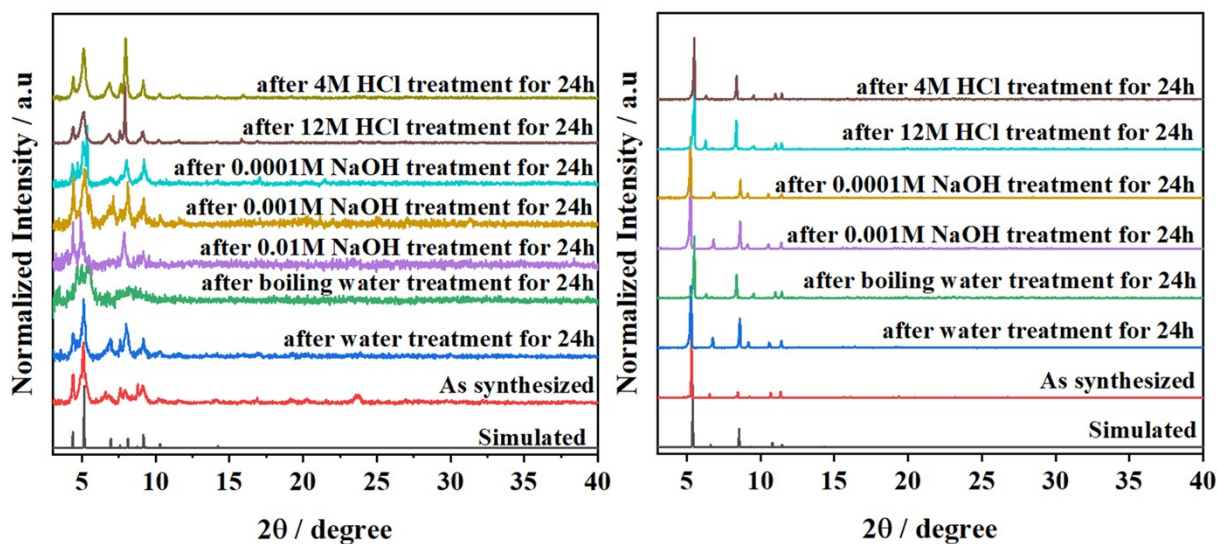


Figure S8. PXR D patterns of simulated, as-synthesized HIAM-4033 (left) and HIAM-4034 (right) and after treatment under different conditions for 24 h.

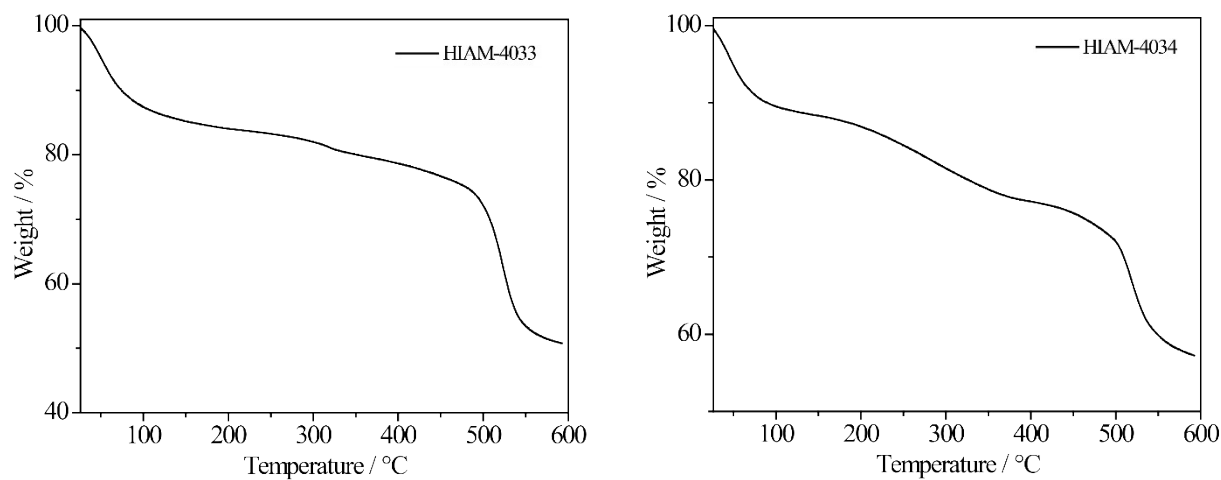


Figure S9. The TGA curves of HIAM-4033 and HIAM-4034.

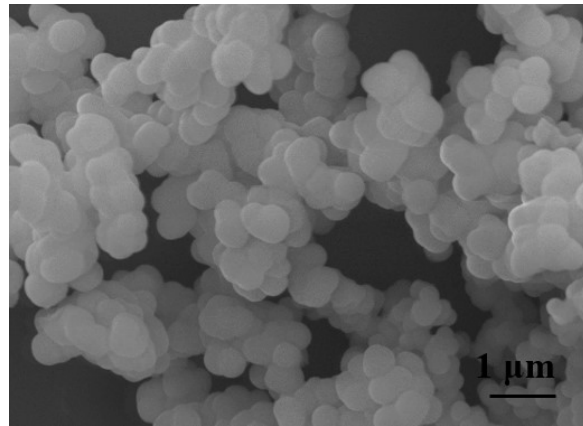


Figure S10. SEM images of nanosized HIAM-4033.

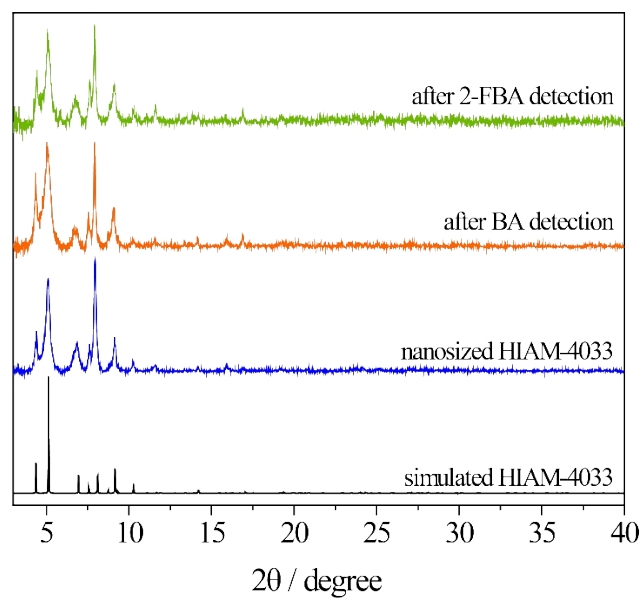


Figure S11. PXRD patterns of simulated, nanosized and after acids detection of HIAM-4033.

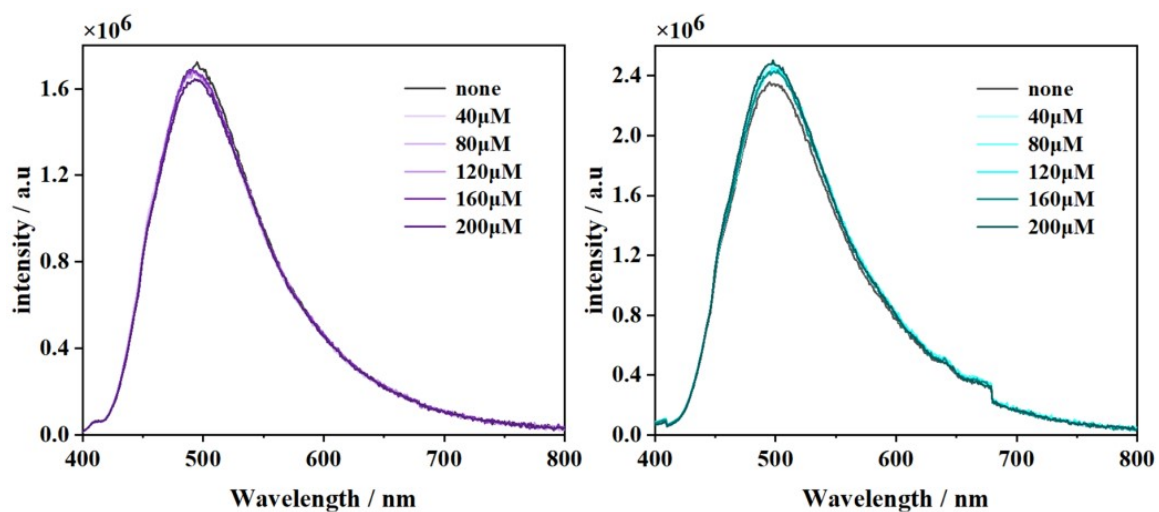


Figure S12. The emission responses of H₃5CIB towards 2-FBA (left) and BA (right) in solution.

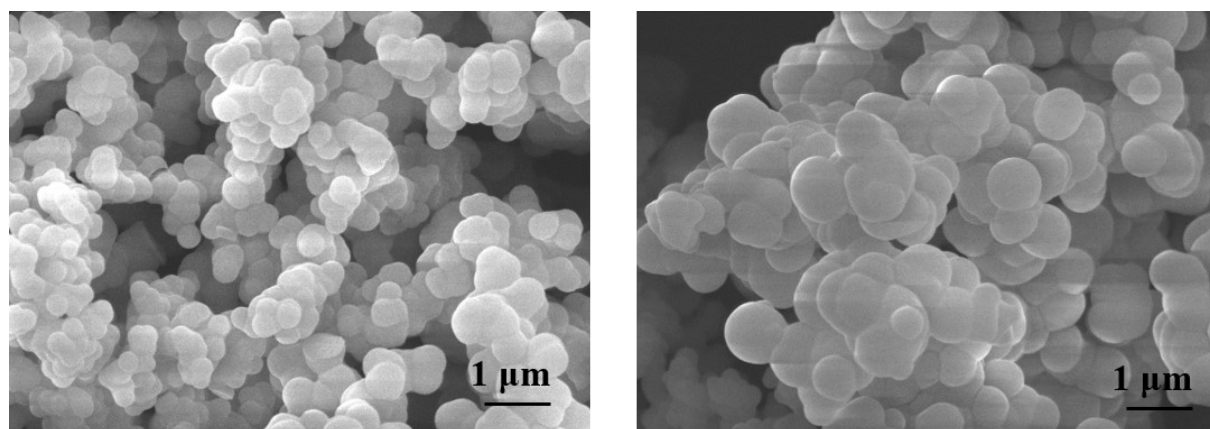


Figure S13. SEM images of nanosized HIAM-4033 after detection of 2-FBA (left) and BA (right).

Table S1. Crystal data and structure refinement for HIAM-4033.

CCDC No.	2269047	
Empirical formula	C ₇₉ H ₅₀ N ₆ O ₃₂ S ₃ Zr ₆	
Formula weight	2238.75	
Temperature	193 K	
Wavelength	1.34139 Å	
Crystal system	trigonal	
Space group	P3 ₁ 21	
Unit cell dimensions	a = 23.3248(9) Å	α = 90°
	b = 23.3248(9) Å	β = 90°
	c = 32.710(2) Å	γ = 120°
Volume	15411.6(15) Å ³	
Z	3	
Density (calculated)	0.724 g/cm ³	
Absorption coefficient	2.011 mm ⁻¹	
F(000)	3330.0	
Crystal size	0.13 x 0.12 x 0.1 mm ³	
Theta range for data collection	3.806 to 105.96°	
Index ranges	-26 ≤ h ≤ 27, -27 ≤ k ≤ 27, -38 ≤ l ≤ 36	
Reflections collected	116666	
Independent reflections	18131 [R(int) = 0.0813, R(sigma) = 0.0492]	
Data / restraints / parameters	18131 / 77 / 645	
Goodness-of-fit on F ²	1.011	
Final R indices [I > 2σ(I)]	R1 = 0.0605, wR2 = 0.1708	
R indices (all data)	R1 = 0.0810, wR2 = 0.1880	
Largest diff. peak and hole	1.34 and -1.29 e.Å ⁻³	

Table S2. Crystal data and structure refinement for HIAM-4034.

CCDC No.	2269048	
Empirical formula	C ₈₆ H ₇₅ N ₉ O ₃₅ S ₃ Zr ₆	
Formula weight	2438.05	
Temperature	193 K	
Wavelength	1.34139 Å	
Crystal system	trigonal	
Space group	R32	
Unit cell dimensions	a = 32.5504(6) Å	α = 90°
	b = 32.5504(6) Å	β = 90°
	c = 40.8188(13) Å	γ = 120°
Volume	37454.4(18) Å ³	
Z	9	
Density (calculated)	0.973 g/cm ³	
Absorption coefficient	2.515 mm ⁻¹	
F(000)	10998.0	
Crystal size	0.13 x 0.11 x 0.1 mm ³	
Theta range for data collection	7.46 to 107.814°	
Index ranges	-39 ≤ h ≤ 38, -39 ≤ k ≤ 35, -46 ≤ l ≤ 49	
Reflections collected	96445	
Independent reflections	15232 [R(int) = 0.1097, R(sigma) = 0.0770]	
Data / restraints / parameters	15232 / 469 / 733	
Goodness-of-fit on F ²	0.982	
Final R indices [I > 2σ(I)]	R1 = 0.0481, wR2 = 0.1206	
R indices (all data)	R1 = 0.0736, wR2 = 0.1336	
Largest diff. peak and hole	0.61 and -0.51 e.Å ⁻³	

References

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. Sheldrick, G.M. SHELXT-Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71*, 3-8.
3. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3-8.