Supporting Information

Metal-organic frameworks (MOFs) as fuels for advanced applications: evaluating and modifying the combustion energy of popular MOFs

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S1. Materials and methods

The compounds 2-butylimidazole, 2-propylimidazole, 2-ethylimidazole, 2methylimidazole, terephthalic acid, 2-aminoterephthalic acid, zirconium(IV) isopropoxide, methyacrylic acid, zinc oxide, ammonium acetate, ammonium sulfate, triethylamine, and cobalt(II) chloride hexahydrate were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used as received. ZIF-8, MIL-53 and HKUST-1 were obtained from Sigma-Aldrich, and an additional sample of ZIF-8 was obtained from ACSYNAM. All MOFs were activated ahead of use.

S1.1. Activation and surface area measurements

All samples were activated by washing with MeOH (30 mL), followed by centrifugation for 20 minutes at 4500 rpm, after which the supernatant was separated from the solid. The process was performed a total of three times, and the samples placed in a vacuum oven at 120 °C (85 °C for UiO-66 and UiO-66-NH₂) overnight. All samples were stored under argon. Nitrogen sorption isotherms of the activated MOFs were measured on a TriStar 3000 instrument, and the experiments were conducted at 77 K.

S1.2. Fourier-transform attenuated total reflectance infrared (FTIR-ATR) spectroscopy

The spectra were recorded using a Bruker Alpha FT-IR spectrometer (Bruker Optics Ltd., Milton, ON, Canada) decorated by diamond crystal in the range of 4000-450 cm⁻¹ and with resolution of 4 cm⁻¹.

S1.3. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted on a TGA/DSC 1 thermal balance (Mettler-Toledo, Columbus, Ohio, USA), with samples of size 2 mg to 10 mg placed in open 70 μ L alumina crucibles. All measurements were done in a dynamic atmosphere of air (gas flow of 25 mL/min), by heating up to 800 °C at a constant heating rate of 10 °C/min.

S1.4. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) data were collected on a Bruker D2 Phaser diffractometer equipped with a LYNXEYE linear position sensitive detector (Bruker AXS, Madison, WI, USA), using Ni-filtered CuKa radiation. A PXRD pattern of ANA-Zn(**Bulm**)₂ suitable for structure elucidation was collected on a Bruker D8 Advance diffractometer equipped with a LYNXEYE-XE linear position sensitive detector (Bruker AXS, Madison, WI), using Ni-filtered CuKa radiation.

Rietveld refinement of the ANA-Zn(**Bulm**)₂ structure (**Table S1**) was performed using the software TOPAS Academic v. 6 (Coelho Software). The structure was refined in the cubic

la-3*d* space group, with diffraction peak shapes described by a pseudo-Voigt function, and the background modelled using a Chebyshev polynomial function. The linker geometry was defined by a rigid body, which was given rotational and translational degrees of freedom, subject to the space group symmetry constraints. Crystallographic data for ANA-Zn(**Bulm**)₂ structure in CIF format was deposited with the CCDC (deposition code 1906483).

The Pawley refinement was used to confirm the agreement of MOF unit cell parameters with the measured X-ray powder patterns. Similarly to Rietveld refinement, Pawley fitting involved pseudo-Voigt peak shapes and Chebyshev polynomial background function.

	ANA-Zn(Bulm) ₂
Formula	Zn(C7H11N2)2
<i>M</i> _r	311.75
Crystal system	cubic
a/Å	26.765(2)
b/Å	26.765(2)
c/Å	26.765(2)
α (°)	90
β (°)	90
γ (°)	90
V/Å ³	19173(4)
Space group	la-3d
ρ _c (g cm ⁻³)	1.296
Radiation type	Cu <i>K</i> α
<i>F</i> (000)	7872
R _{wp}	0.139
R _p	0.097
R_{Bragg}	0.076
Х ²	9.325

Table S1. Crystallographic and general data for the structure of ANA-Zn(Bulm)₂ determined from powder X-ray diffraction data.

S1.5. Combustion Calorimetry

The combustion calorimetry measurements were carried out on a 6200 Isoperibol Calorimeter (Parr Instrument Company, Moline, IL), which is a microprocessor controlled, isoperibol oxygen bomb calorimeter. The combustion calorimeter was calibrated by benzoic acid and all measurements were carried out on a scale of 0.5 grams and repeated three times. The combustion calorimetry experiment is conducted at constant volume, providing a measurement of changes in internal energy. Enthalpies were calculated from internal energies measured by combustion calorimetry by taking into consideration the difference in the amount of gaseous components (Δ n) between reactants and products of the combustion reactions.

$$\Delta U^{0} = \Delta H^{0} - \Delta n R T$$

The combustion reactions for each MOF are provided below:

Zn(MeIm)₂: Zn(C₈H₁₀N₄)_(s) + 11 O_{2(g)} → ZnO (s) + 8 CO_{2(g)} + 5 H₂O_(l) + 2 N_{2(g)} (Δn = -1)

Co(Melm)₂: Co(C₈H₁₀N₄)_(s) + 11.16 O_{2(g)} → 0.33Co₃O_{4 (s)} + 8 CO_{2(g)} + 5 H₂O_(l) + 2 N_{2(g)} (Δn = -1.16)

 $Zn(EtIm)_{2}: Zn(C_{10}H_{14}N_{4})_{(s)} + 14 O_{2(g)} \rightarrow ZnO_{(s)} + 10 CO_{2(g)} + 7 H_{2}O_{(l)} + 2 N_{2(g)} (\Delta n = -2)$

 $Zn(PrIm)_{2}: Zn(C_{12}H_{18}N_{4})_{(s)} + 17 O_{2(g)} \rightarrow ZnO_{(s)} + 12 CO_{2(g)} + 9 H_{2}O_{(l)} + 2 N_{2(g)} (\Delta n = -3)$

 $Zn(\textbf{Bulm})_{2}: Zn(C_{14}H_{22}N_{4})_{(s)} + 20 \text{ } O_{2(g)} \rightarrow ZnO_{(s)} + 14 \text{ } CO_{2(g)} + 11 \text{ } H_{2}O_{(l)} + 2 \text{ } N_{2(g)} (\Delta n = -4)$

HKUST-1: Cu(C₆H₂O₄)_(s) + 5 O_{2(g)} → CuO_(s) + 6 CO_{2(g)} + H₂O_(l) (Δn = +1)

MIL-53(AI): AI(C₈H₅O₅)_(s) + 7.5 O_{2(g)} \rightarrow 0.5 AI₂O_{3(s)} + 8 CO_{2(g)} + 2.5 H₂O_(l) (Δn = +0.5)

UiO-66: $Zr(C_8H_{4.57}O_{5.33})_{(s)}$ + 7.5 $O_{2(g)}$ → $ZrO_{2(s)}$ + 8 $CO_{2(g)}$ + 2.33 $H_2O_{(I)}$ (Δn = +0.5)

UiO-66-NH₂: Zr(C₈H_{5.67}NO_{5.33})(s) + 7.75 O_{2(g)} → ZrO_{2(s)} + 8 CO_{2(g)} + 2.83 H₂O_(l) + 0.5 N_{2(g)} (Δ n = +0.75)

S2. Synthesis

The MOFs were prepared using either solution synthesis (ZIF-67), or modifications of previously reported mechanochemical ion- and liquid-assisted grinding¹ (ILAG, for *dia*-Zn(**Melm**)₂, *qtz*-Zn(**EtIm**)₂, ANA-Zn(**EtIm**)₂, ANA-Zn(**PrIm**)₂, ANA-Zn(**BuIm**)₂) or accelerated aging methods^{2,3} (UiO-66, UiO-66-NH₂, ANA-Zn(**EtIm**)₂). Details are provided below.

SOD-Co(**MeIm**)₂ (ZIF-67) was made by dissolving 2-methylimidazole (H**MeIm**, 22 mmol) and triethylamine (22 mmol) in 80 mL of EtOH, followed by addition of a solution of $CoCl_{2}\cdot 6H_{2}O$ (10 mmol) in 100 mL of EtOH over one hour. The solution was stirred for additional 2 hours and left at ambient conditions for overnight without stirring. The precipitation was filtered, washed twice of 100 mL of EtOH. Yield 45%.

dia-Zn(**MeIm**)₂ was obtained by ball milling of a mixture of H**MeIm** (2.1 mmol), ZnO (1 mmol) and ammonium acetate (5 mmol%) in a 10 mL stainless steel milling jar, using one stainless steel milling ball of 10 mm diameter. The reaction mixture was milled for 45 minutes at a milling frequency of 30 Hz, after which the product was washed with 30 mL water, and then three times with 30 mL of MeOH.

RHO-Zn(**EtIm**)₂ was made using a modification of the previously published aging procedure, wherein 2-ethylimidazole (H**EtIm**, 30 mmol), ZnO (10 mmol) and adipic acid (2 mmol% with respect to ZnO) were mixed well and aged for 2 days in a Petri dish at 100% relative humidity and 45 °C. After two days the product was washed three times with 300 mL of ethanol and isolated.

ANA-Zn(**EtIm**)₂ was made by milling a solid mixture of ZnO (814 mg, 10 mmol), 2ethylimidazole (2018.7 mg, 21 mmol) and catalytic ammonium acetate (77 mg, 1 mmol) in a 50 mL stainless steel jar, aloing with 1 mL of benzene. The reaction mixture was milled for 30 min using two stainless steel balls of 10 mm diameter. The product was subsequently washed with MeOH and evacuated.

qtz-Zn(**EtIm**)₂ was made by milling a solid mixture of ZnO (814 mg, 10 mmol), 2ethylimidazole (2018.7 mg, 21 mmol) and catalytic NH₄NO₃ (100 mg, 1.25 mmol), placed in a 50 mL stainless steel jar with two 10 mm diameter stainless steel balls and 1 mL of DMF. The reaction mixture was then milled for 40 min. The product was subsequently washed with MeOH and evacuated.

ANA-Zn(**PrIm**)₂ was made by milling a solid mixture of ZnO (814 mg, 10 mmol), 2propylimidazole (2313.3 mg, 21 mmol) and catalytic ammonium acetate (77 mg, 1 mmol) in a 50 mL stainless steel jar, with the addition of 1 mL of ethanol. The reaction mixture was milled for 30 min using two stainless steel balls of 10 mm diameter. The product was subsequently washed with MeOH and evacuated.

ANA-Zn(**Bulm**)₂ was made by milling a solid mixture of ZnO (814 mg, 10 mmol), 2butylimidazole (2608 mg, 21 mmol) and catalytic ammonium acetate (77 mg, 1 mmol), placed in a 50 mL stainless steel along with 1 mL of ethanol. The reaction mixture was then milled for 30 minutes using two stainless steel balls of 10 mm diameter. The product was subsequently washed with MeOH and evacuated.

UiO-66 and UiO-66-NH₂ were made following a previously reported procedure from the Zr₆ methacrylate cluster (1.0 grams)¹ and H₂**BDC** (for UiO-66, 0.58 grams) or H₂**BDC**-**NH**₂ (for UiO-66-NH₂, 0.62 grams). The reactants were mixed in a 1:6 respective stoichiometric ratio, briefly milled for two minutes in a Retsch MM400 mixer mill operating at 30 Hz to prepare a homogeneous mixture, and then dispersed in a Petri dish and left to age in an atmosphere of MeOH vapor at 45 °C. Highly crystalline samples (based on PXRD analysis) of UiO-66 and UiO-66-NH₂ were obtained within 7 days, washed with MeOH followed by centrifugation up to five times, and finally dried in vacuum oven at 85 °C for 2 hours. The procedure yielded 1.0 g of UiO-66 and 1.15 g of UiO-66-NH₂.



S3. Surface area measurements (BET)

Figure S1. Nitrogen sorption isotherm measured at 77K for ZIF-8 (purchased from Sigma-Aldrich) (BET surface area of 1350 m²/g)



Figure S2. Nitrogen sorption isotherm measured at 77K for ZIF-8 (purchased from ACSYNAM) with BET surface area of 1352 m^2/g



Figure S3. Nitrogen sorption isotherm measured at 77K for SOD-Co(MeIm)₂ with BET surface area of 1510 m^2/g



Figure S4. Nitrogen sorption isotherm measured at 77K for RHO-Zn(EtIm)_2 with BET surface area of 1210 m^2/g



Figure S5. Nitrogen sorption isotherm measured at 77K for ANA-Zn(EtIm)_2 with BET surface area of 610 m^2/g



Figure S6. Nitrogen sorption isotherm measured at 77K for ANA-Zn(PrIm)₂ with BET surface area of 440 m^2/g



Figure S7. Nitrogen sorption isotherm measured at 77K for MIL-53 (purchased from Sigma-Aldrich) with BET surface area of 950 m^2/g .



Figure S8. Nitrogen sorption isotherm measured at 77K for HKUST-1 (Purchased from Sigma-Aldrich) with BET surface area of 1340 m^2/g



Figure S9. Nitrogen sorption isotherm measured at 77K for UiO-66 with BET surface area of 870 m^2/g .



Figure S10. Nitrogen sorption isotherm measured at 77K for UiO-66-NH₂ with BET surface area of 960 m^2/g





Figure S11. TGA (*blue curve*) and DSC (*orange curve*) thermograms for ZIF-8 (purchased from Sigma-Aldrich) with residue of 37.9% (calc. 35.8%).



Figure S12. TGA (*blue curve*) and DSC (*orange curve*) thermograms of ZIF-8 (obtained from ACSYNAM) with residue of 37.5% (calc. 35.8%).



Figure S13. TGA (*blue curve*) and DSC (*orange curve*) thermograms of *dia*-Zn(**MeIm**)₂ with residue of 35.7% (calc. 35.7%).



Figure S14. TGA (*blue curve*) and DSC (*orange curve*) thermograms of SOD-Co(**Melm**)₂ (ZIF-67) with residue of 38.1% (calc. 36.3%).



Figure S15. TGA (*blue curve*) and DSC (*orange curve*) thermograms of RHO-Zn(**EtIm**)₂ with residue of 33.4% (calc. 31.8%).



Figure S16. TGA (*blue curve*) and DSC (*orange curve*) thermograms of ANA-Zn(**EtIm**)₂ with residue of 33.0% (calc. 31.8%).



Figure S17. TGA (*blue curve*) and DSC (*orange curve*) thermograms of *qtz*-Zn(**EtIm**)₂ with residue of 33.1% (calc. 31.8%).



Figure S18. TGA (*blue curve*) and DSC (*orange curve*) thermograms of ANA-Zn(**PrIm**)₂ with residue of 29.4% (calc. 28.7%).



Figure S19. TGA (*blue curve*) and DSC (*orange curve*) thermograms of ANA-Zn(**Bulm**)₂ with residue of 26.1% (calc. 26.2%).



Figure S20. TGA (*blue curve*) and DSC (*orange curve*) thermograms of MIL-53 (Aldrich) with residue of 26.0% (calc. 24.5%).



Figure S21. TGA (*blue curve*) and DSC (*orange curve*) thermograms of HKUST-1 (Aldrich) with residue of 32.6% (calc. 32.6%).



Figure S22. TGA (*blue curve*) and DSC (*orange curve*) thermograms of UiO-66 with residue of 35.8% (calc. 35.4%).



Figure S23. TGA (*blue curve*) and DSC (*orange curve*) thermograms of UiO-66-NH₂ with residue of 34.4% (calc. 33.9%).



S5. Powder X-ray diffraction and Pawley refinement plots

Figure S24. Overlay of PXRD patterns for ZIF-8 (obtained from Sigma-Aldrich) before and after activation.



Figure S25. Final Pawley refinement plot for ZIF-8 (obtained from Sigma-Aldrich) after activation.



Figure S26. Overlay of PXRD patterns for ZIF-8 after activation (obtained from ACSYNAM) before and after activation.



Figure S27. Final Pawley refinement plot for ZIF-8 after activation (obtained from ACSYNAM).



Figure S28. Overlay of PXRD patterns for SOD-Co(MeIm)₂ (ZIF-67) before and after activation.



Figure S29. Final Pawley refinement plot for SOD-Co(Melm)₂ (ZIF-67) after activation.



Figure S30. Overlay of PXRD patterns for *dia*-Zn(Melm)₂ after washing and evacuation.



Figure S31. Final Pawley refinement plot for *dia*-Zn(Melm)₂ after activation.



Figure S32. Overlay of PXRD patterns for RHO-Zn(EtIm)₂ before and after activation.



Figure S33. Final Pawley refinement plot for RHO-Zn(EtIm)₂ after activation.



Figure S34. Overlay of PXRD patterns for PXRD of ANA-Zn(EtIm)₂ before and after activation.



Figure S35. Final Pawley refinement plot for ANA-Zn(EtIm)₂ after activation.



Figure S36. Overlay of PXRD patterns for *qtz*-Zn(EtIm)₂ after washing and drying.



Figure S37. Final Pawley refinement plot for *qtz*-Zn(EtIm)₂ after activation.



Figure S38. Overlay of PXRD patterns for ANA-Zn(PrIm)₂ before and after activation.



Figure S39. Final Pawley refinement plot for ANA- $Zn(Prlm)_2$ after activation.



Figure S40. Overlay of PXRD patterns for ANA-Zn(Bulm)₂ before and after activation.



Figure S41. Overlay of PXRD patterns for HKUST-1 (obtained from Sigma-Aldrich) before and after activation.



Figure S42. Final Pawley refinement plot for HKUST-1 after activation (obtained from Sigma-Aldrich).



Figure S43. Overlay of PXRD patterns for MIL-53(AI) (purchased from Sigma-Aldrich) before and after activation.



Figure S44. Final Pawley refinement plot for of MIL-53(Al) after activation (obtained from Sigma-Aldrich).



Figure S45. Overlay of PXRD patterns for UiO-66 before and after activation



Figure S47. Overlay of PXRD patterns for UiO-66-NH₂ before and after activation.





S6. Infrared spectroscopy

Figure S49. Overlay of FTIR-ATR spectra of herein studied MOFs, after washing and evacuation in a vacuum oven.

S7. Analysis of specific energy with respect to framework density and composition



Figure S50. Change in measured E_g with respect to weight fraction of carbon in the explored MOFs.



Figure S51. Change in measured E_g with respect to weight fraction of hydrogen in the explored MOFs.



Figure S52. Change in measured E_g with respect to weight fraction of nitrogen in the explored MOFs.



Figure S53. Change in measured E_g with respect to weight fraction of oxygen in the explored MOFs.



Figure S54. Change in measured E_g with respect to weight fraction of the metal (Zn, Co, Cu, Al or Zr) in the explored MOFs.



Figure S55. Dependence of E_g on framework density (expressed as number of tetrahedral nodes per unit volume, T/nm³) for selected ZIFs.

S8. Crystal structure of ANA-Zn(Bulm)₂



Figure S56. Structure of ANA-Zn(**Bulm**)₂ viewed down the crystallographic (111)direction, illustrating surface area accessible to a probe of 3.0 Å diameter.

S9. Comparison of energy density (E_v) and specific energy (E_g)



Figure S57. Comparison E_v vs E_g of the herein explored MOFs with known or proposed liquid and solid fuels.

S10. References

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