Electronic Supplementary Material (ESI) for Materials Advances.

— Supplementary Information —

Adsorption Properties of Acetylene, Ethylene and Ethane in UiO-66 with Linker Defects and NO_2 Functionalization

H. Pandey,[1,2] T. Barrett,[2,3] M. D. Gross,[2,4] and T. Thonhauser[1,2]

[1] *Department of Physics, Wake Forest University, Winston-Salem, NC 27109, USA.*
[2] *Center for Functional Materials, Wake Forest University, Winston-Salem, NC 27109, USA.*
[3] *Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109, USA.*
[4] *Department of Engineering, Wake Forest University, Winston-Salem, NC 27109, USA.*

I. ADDITIONAL FIGURES AND TABLES

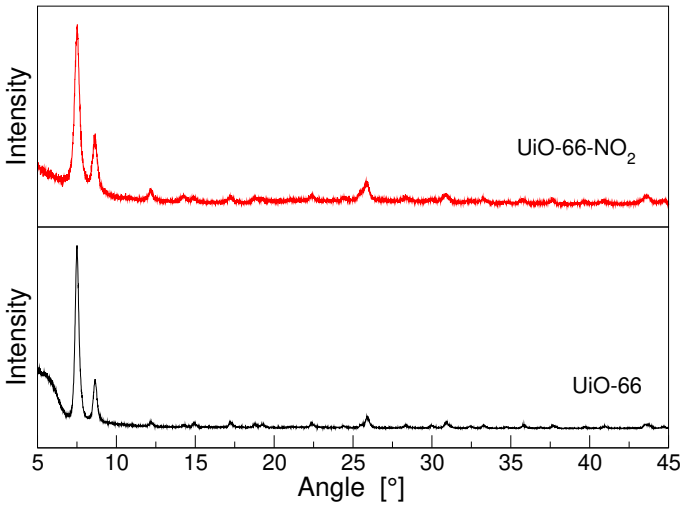

FIG. S1. Powder X-ray diffraction patterns were collected with a Bruker D2 Phaser X-ray diffractometer using CuKα radiation. The 2θ value range was 5° to 45°, the 2θ increment was 0.01°, the time step was 0.1 s, and the stage was rotated at 1 revolution per minute. The results confirm the formation of the crystalline UiO-66 phase as reported in the literature.[1]

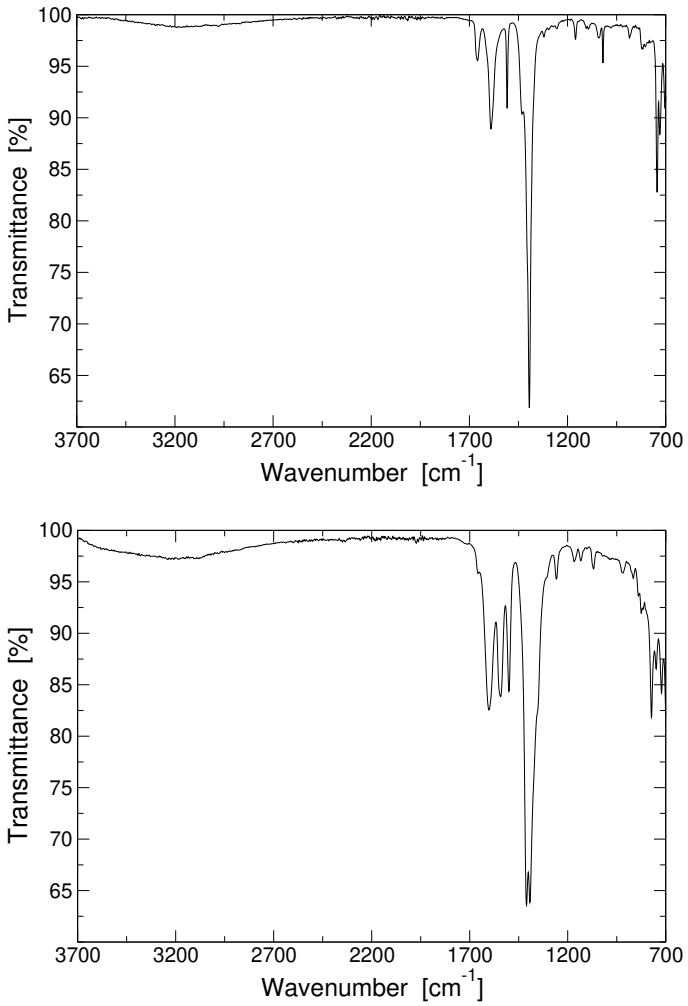

FIG. S2. A Perkin Elmer 100 FTIR spectrometer was used to probe the bond vibrations of UiO-66 and UiO-66–NO_2. Powders of each sample were directly placed on the IR holder and pressed with a built-in press. The IR spectrum was acquired between 650 and 4000 cm^{-1}. Both results match previously reported IR spectra[1] and confirm the presence of NO_2 in UiO-66–NO_2.

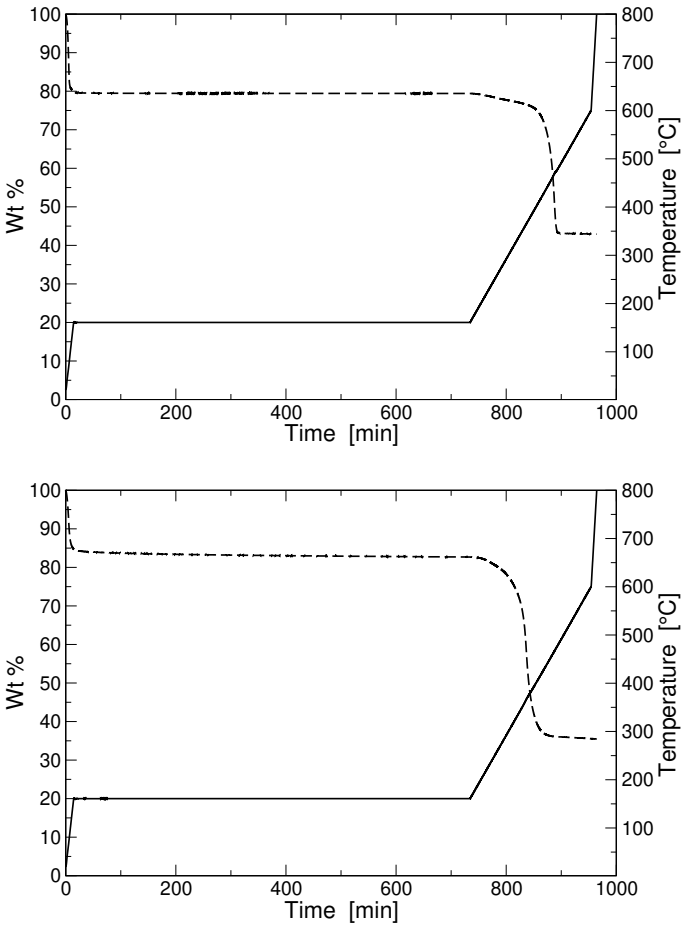

FIG. S3. Thermogravimetric analysis (SDT Q600, TA Instruments) was used to investigate the number of missing linker defects in UiO-66 and UiO-66–NO_2. Samples were heated from ambient temperature to 160 °C at a ramp rate of 10 °C/min, held at 160 °C for 12 h, heated to 600 °C at a ramp rate of 2 °C/min, and then heated to 800 °C at a ramp rate of 10 °C/min. The hold at 160 °C was used to activate the sample prior to decomposition. The final weight was assumed to be ZrO_2, which was confirmed by X-ray diffraction. The number of missing linker defects was calculated using the activated weight and final weight.

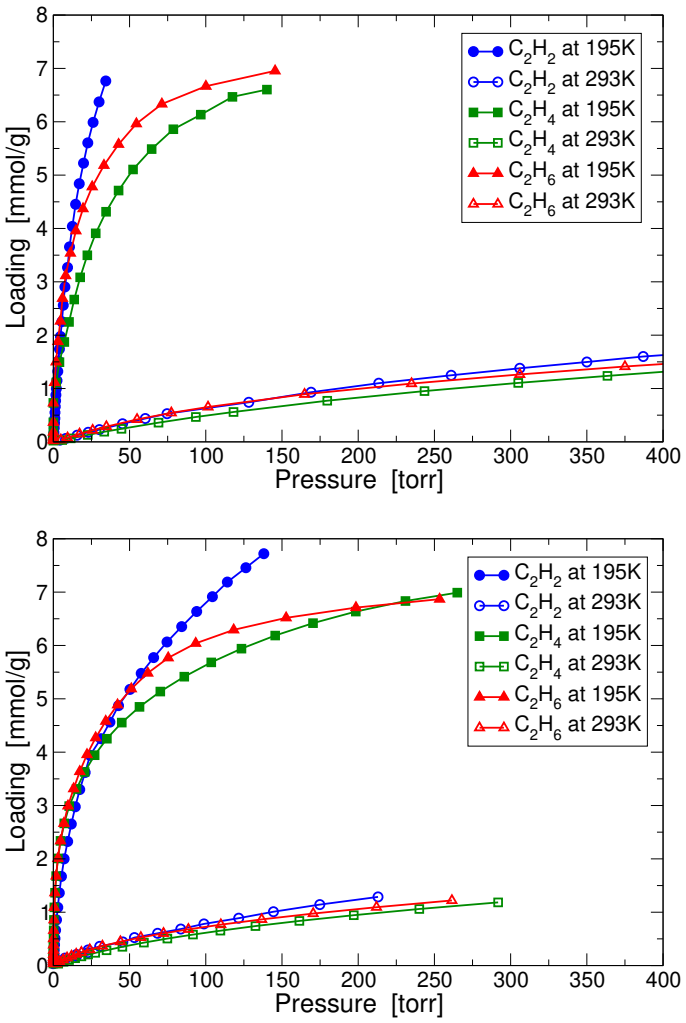

FIG. S4. C_2H_2, C_2H_4 and C_2H_6 isotherms for UiO-66 and UiO-66–NO_2 at 195 K and 293 K.

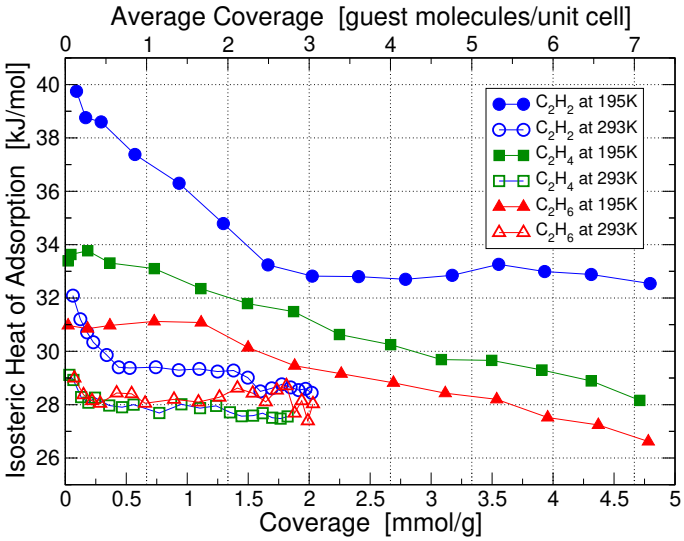

FIG. S5. Isosteric heats of adsorption of C_2H_2, C_2H_4 and C_2H_6 in UiO-66(Zr) at 195 K and 293 K, obtained by calorimetry measurements.

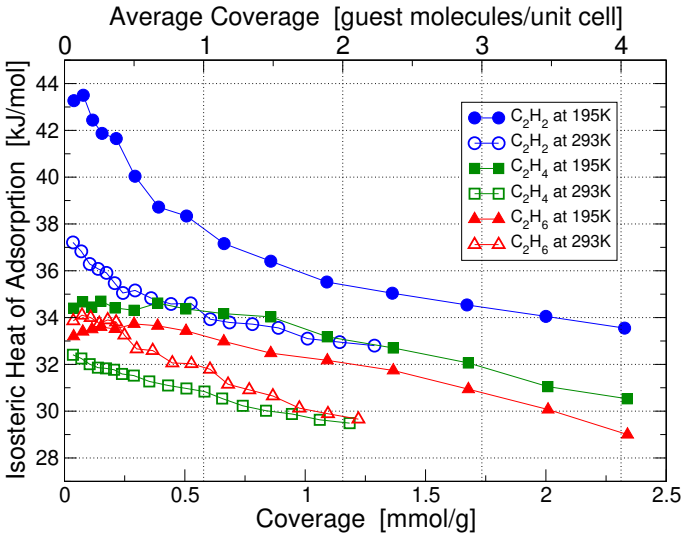

FIG. S6. Isosteric heats of adsorption of C_2H_2, C_2H_4 and C_2H_6 in UiO-66(Zr)–NO_2 at 195 K and 293 K, obtained by calorimetry measurements.

TABLE S1. Experimentally determined average number of linkers per unit cell and BET specific surface area for UiO-66(Zr) and UiO-66(Zr)–NO_2. Theoretical BET specific surface areas as a function of linkers per unit cell are shown for comparison.[2]

		linkers per unit cell	BET surface area ($m^2 \cdot g^{-1}$)
UiO-66	experiment	4.61	1292
	theory	4	800
		6	1550
UiO-66–NO_2	experiment	5.20	831
	theory	4	500
		6	1100

[1] M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, and K. P. Lillerud, Chem. Mater. **22**, 6632 (2010).
[2] M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp, and O. K. Farha, Chem. Commun. **49**, 9449 (2013).