Supporting Information

Observation of Olefin/Paraffin Selectivity in Azo Compound and Its Application into a Metal-Organic Framework

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<Experimental details>

NMR

MIL-101(Cr) and MIL-101(Cr)_DAA samples were digested for nuclear magnetic resonance (NMR) spectroscopy measurements. Activated samples were immersed in 2 M NaOH solutions and then were ultrasonicated for 30 min. From the resulting slurries, water was removed through evaporation. The resulting powders were immersed in dimethyl sulfoxide-d6 (Sigma Aldrich). After the remaining crystals were excluded by a syringe filter, MIL-101(Cr) and MIL-101(Cr)_DAA samples were digested for nuclear magnetic resonance (NMR) spectroscopy measurements.

Breakthrough experiments

The breakthrough experiments were carried out in a custom-built fixed-bed experimental set up. Four mass flow controllers (0~100 ml/min) (Bronkhorst, Germany) were used to regulate the gas flow rates. Three of them were used for pure propylene, propane and helium streams, which were mixed well with each other by flowing through a gas mixer. The first combination made helium/propylene/propane mixtures and the other one was used for the helium stream for in situ regeneration of the adsorbent packed in the column. The column was placed in a ventilated thermostatic oven for measurements at a constant temperature. The composition of the gas flow at the outlet of the column was measured online with a Max300-LG mass spectrometer (Extrel, USA). To avoid large pressure drops, the powder sample was pelletized using a Carver press (Carver, Inc., USA). As-synthesized powders were put into a die with an inner diameter of 13 mm and pressed at 0.5 ton for approximately 1 min. The obtained solid disk was then crushed and sieved to obtain binderless pellets with a size of 500~1000 μm. The pellets were initially activated at 423 K for 12 h under vacuum. The activated pellets were then packed into a stainless-steel column with a length of

15 cm and an internal diameter of 0.44 cm. The column was then degassed by a He flow of 100 ml/min at 423 K for 60 min to remove all the impurities adsorbed during the packing procedure. All the experiments were carried out at 303 K and 1 bar. Before each measurement, a He flow of 100 ml/min at 303 K was introduced into the column for at least 20 min. At t = 0, the He flow was switched to a flow of helium/propylene/propane mixture (helium/propylene/propane = 92/4/4, total flow rate = 100 ml/min).

Table S1. Elemental analyses for MIL-101(Cr) and MIL-101(Cr)_DAA

	C (%)	N (%)	N/C from EA	N/C from NMR
MIL-101(Cr)	39.2	ND*	0	0
MIL-101(Cr)_DAA	35	1.94	0.0554	0.0718

* Not detected.

Table S2. Comparisons with other benchmark adsorbents.

Adsorbent	q (mmol/g) at 100 kPa		$q(C_3H_6)$ /$q(C_3H_8)$	IAST selectivity (50:50) [4]	Working capacity (mmol/g)	Ref
	C_3H_6	C_3H_8			10-100 kPa	
Zeolite 13X [1]	3.44	3.03	1.14	12.6	0.42	[1]
HKUST-1 [1]	6.63	5.81	1.14	3.3	1.7	[2]
Cu(0.6)@MIL-100(Fe) [1]	4.52	3.37	1.34	11.7	1.52	[3]
Co-MOF-74 [2]	7.34	5.48	1.33	37.1	0.74	[4]
Mn-MOF-74 [2]	7.09	5.4	1.31	21.2	1.52	[4]
MIL-101(Cr)_DAA [3]	**7.60**	**6.55**	**1.16**	**4.6**	**5.33**	**This work**

[1] calculated at 323 K

[2] calculated at 298 K
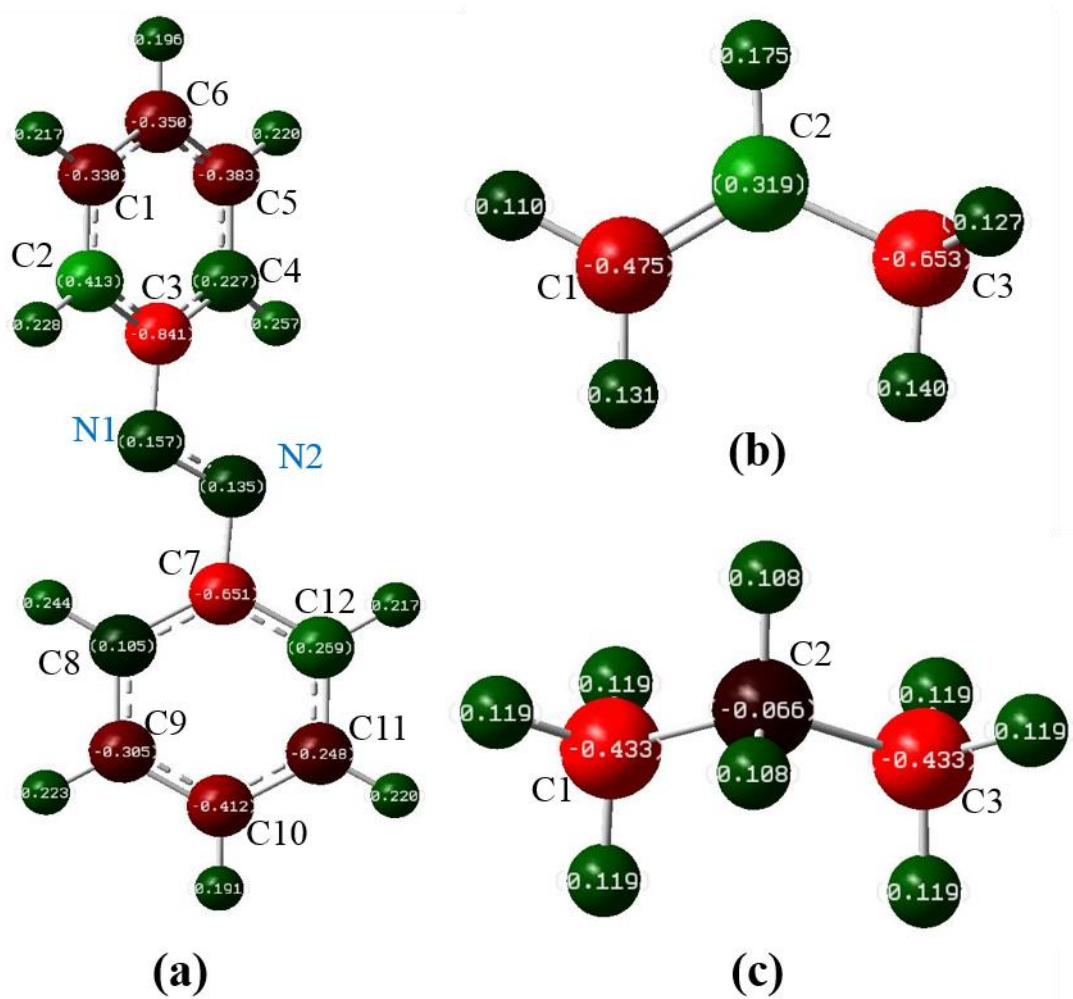
[3] calculated at 303 K

[4] calculated at 30 kPa

Figure S1. Atomic charge distributions of individual molecules; (a) azobenzene, (b) propylene, (c) propane.
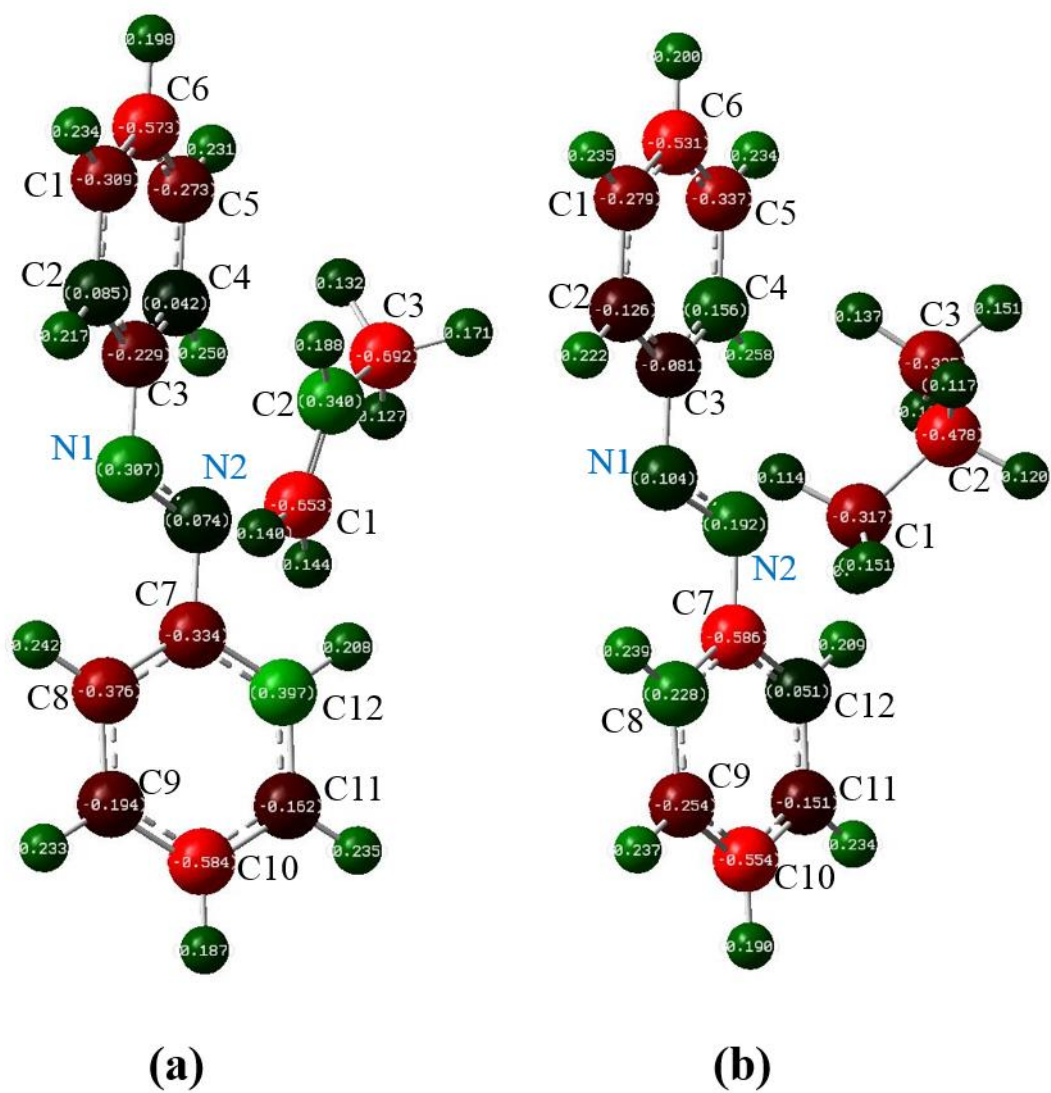
Figure S2. Atomic charge distributions of complexes; (a) azobenzene - propylene, (b) azobenzene - propane. In both structures, N1 and C1 are the closest atoms between Azob and propylene or propane.
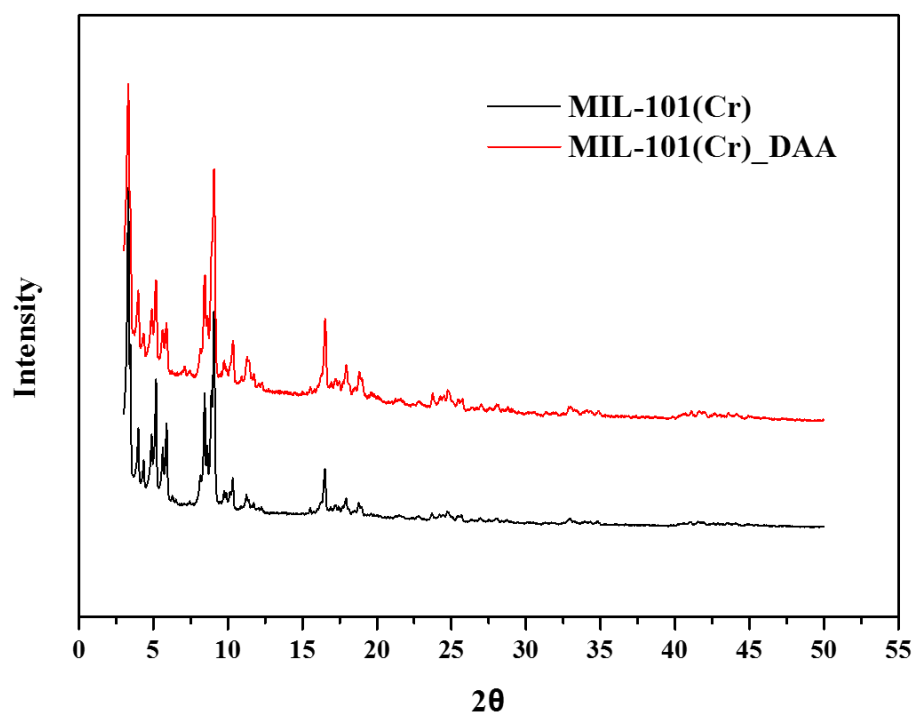
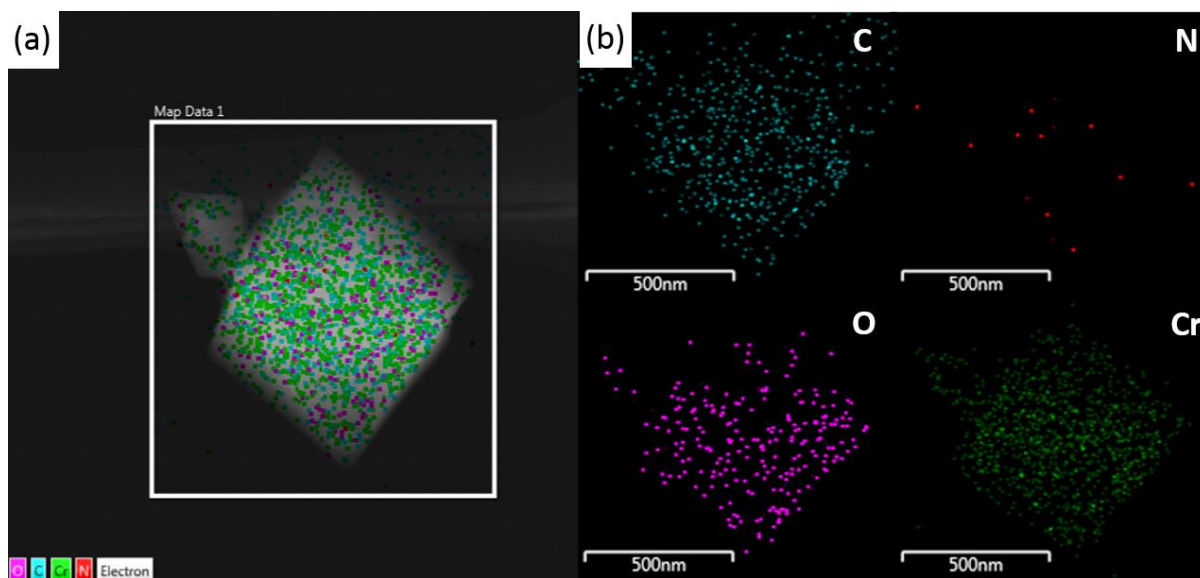**Figure S3.** PXRD patterns for MIL-101(Cr) and MIL-101(Cr)_DAA.

Figure S4. (a) A STEM image of MIL-101(Cr) and (b) corresponding EDS mappings of C (cyan), N (red), O (purple) and Cr (green).
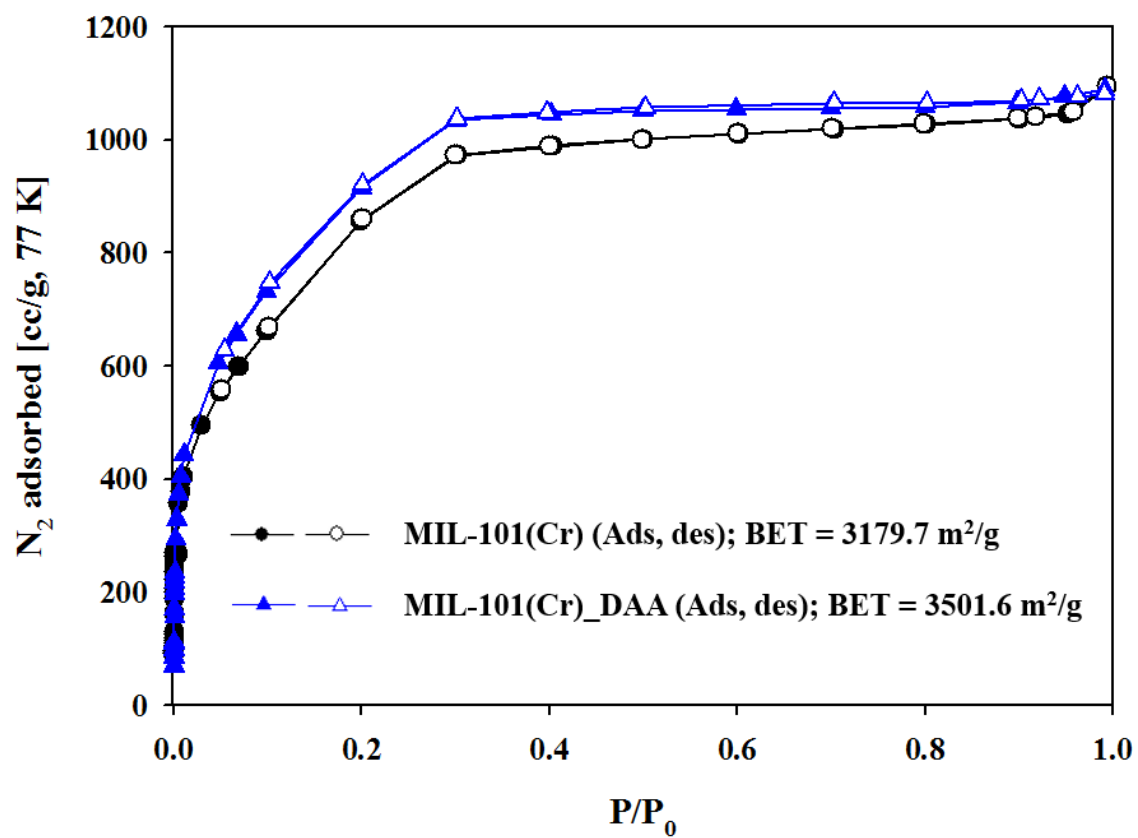
Figure S5. N_2 isotherms of MIL-101(Cr) and MIL-101(Cr)_DAA at 77 K. Calculated BET surface areas are also given in the figure.
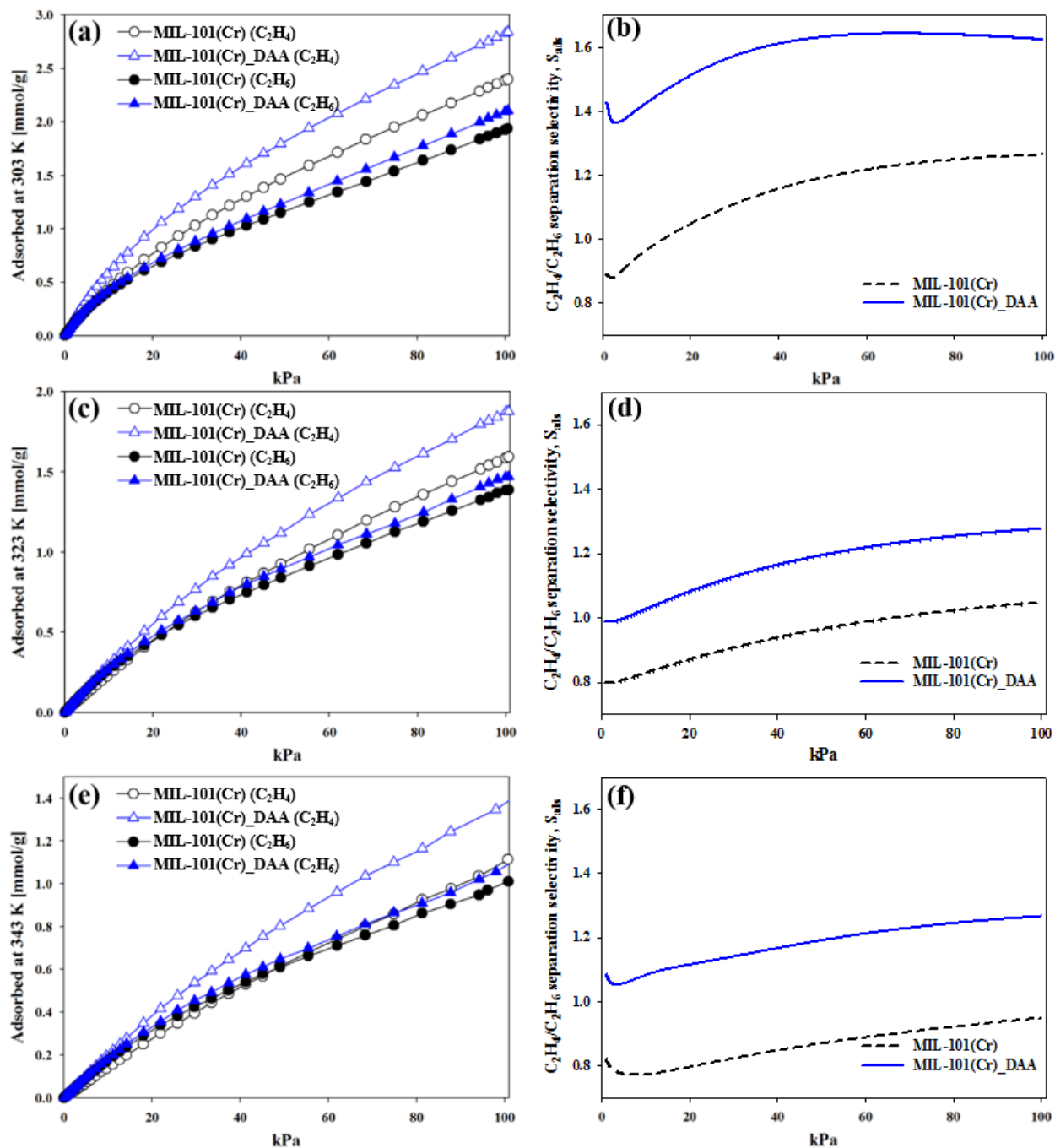
Figure S6. Single component gas adsorption isotherms of MIL-101(Cr) and MIL-101(Cr)_DAA for ethylene and ethane at (a) 303 K, (c) 323 K and (e) 343 K. IAST-predicted ethylene/ethane selectivities at (b) 303 K, (d) 323 K and (f) 343 K.

Reference

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