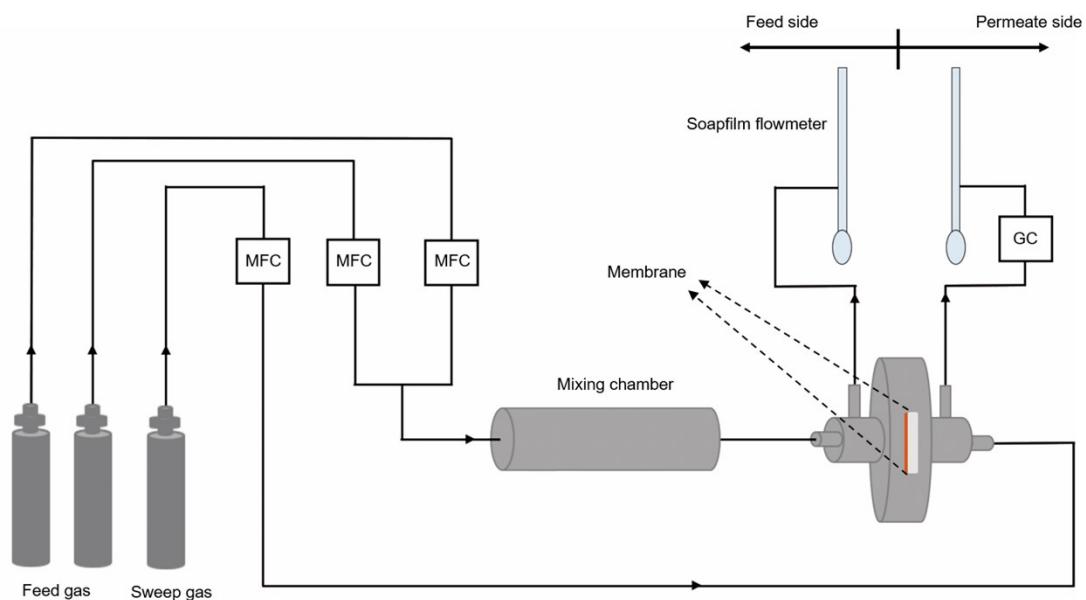


Switchable Molecular Sieving of Capping Metal Organic Framework Membrane

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Scheme S1. Schematic illustration of gas separation set-up (MFC: Mass flowmeter controller; GC: Gas chromatograph).

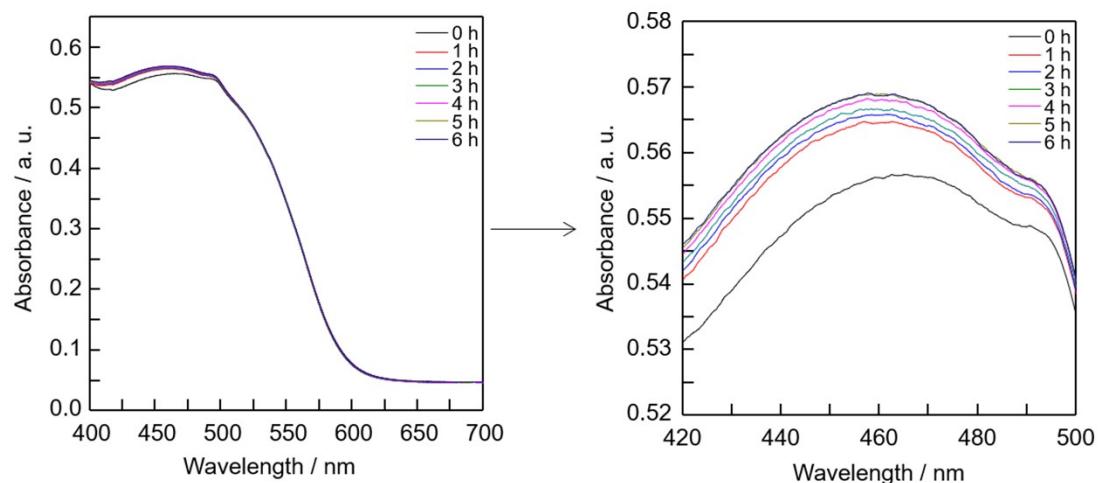


Figure S1. UV-visible spectra of UiO-68-azo after exposure to UV light (365 nm) for different time.

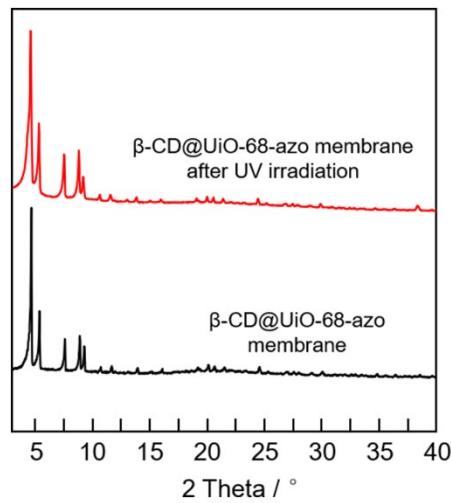


Figure S2. The XRD patterns of UiO-68-azo before (black) and after (red) UV irradiation.

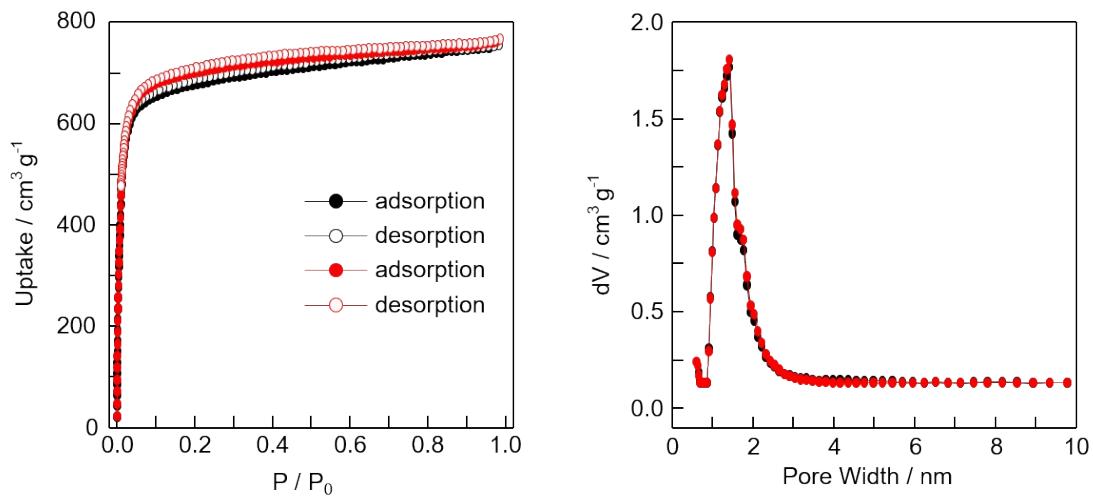


Figure S3. The N₂ sorption isotherm and pore size distribution of UiO-68-azo (black) and UiO-68-azo after UV irradiation (red). The BET surface area and pore size are 2629 m² g⁻¹, 2717 m² g⁻¹ and 1.41 nm, 1.41nm respectively.

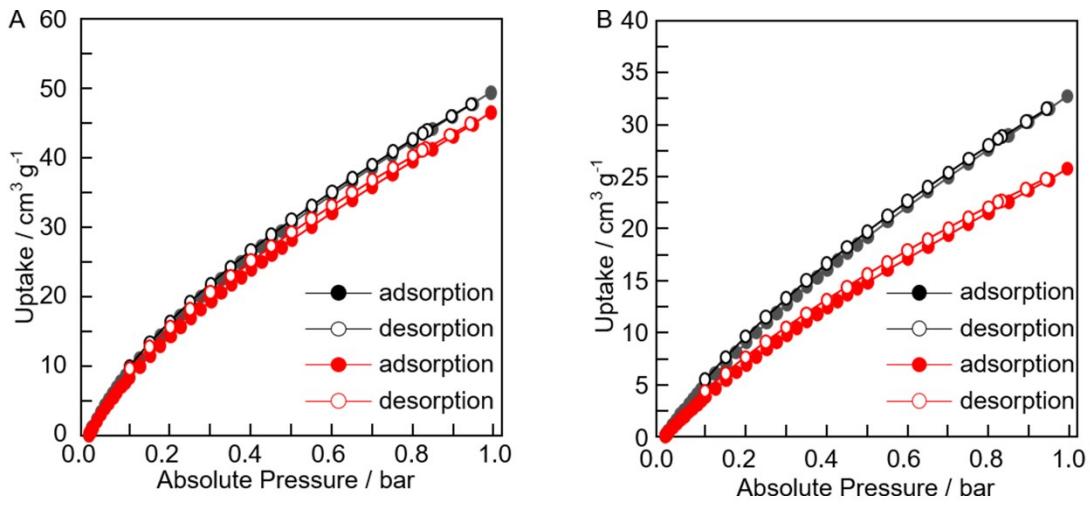


Figure S4. The CO₂ sorption isotherms of UiO-68-azo (black) and UiO-68-azo after UV irradiation (red) at A) 273 K and B) 298 K.

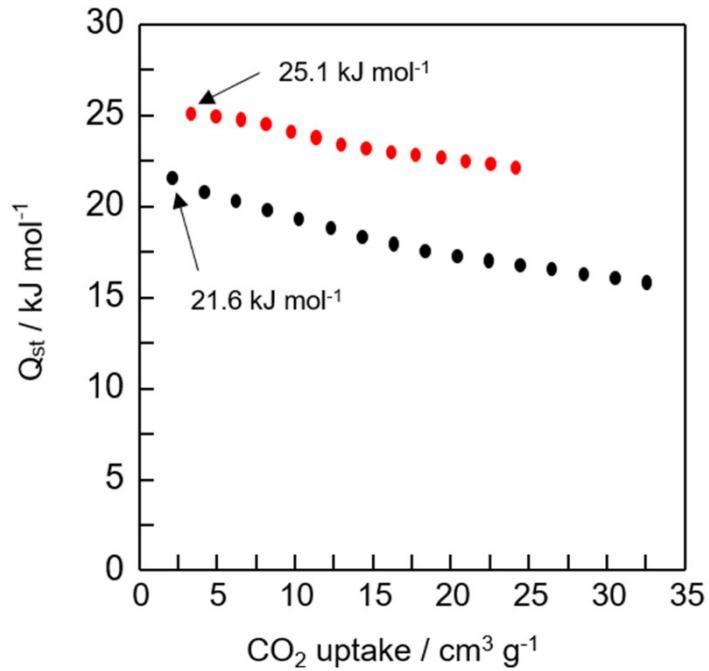


Figure S5. The isosteric enthalpy Q_{st} of CO₂ for UiO-68-azo (black) and UiO-68-azo after UV irradiation (red). The Q_{st} are 21.6 kJ mol⁻¹ and 25.1 kJ mol⁻¹ respectively.

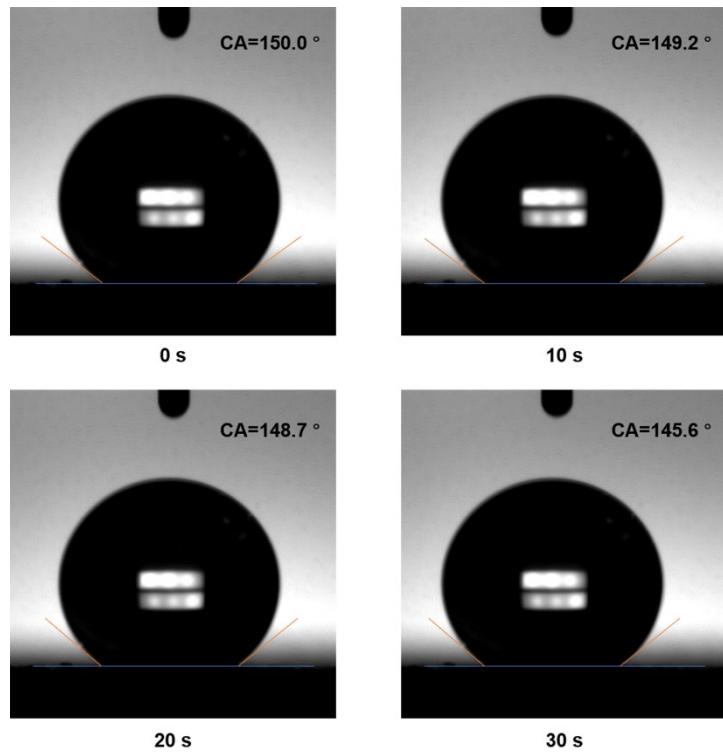


Figure S6. Droplet profiles with inserted static contact angle (CA) value (upper-right corner) on the UiO-68-azo membrane surface at different measuring time.

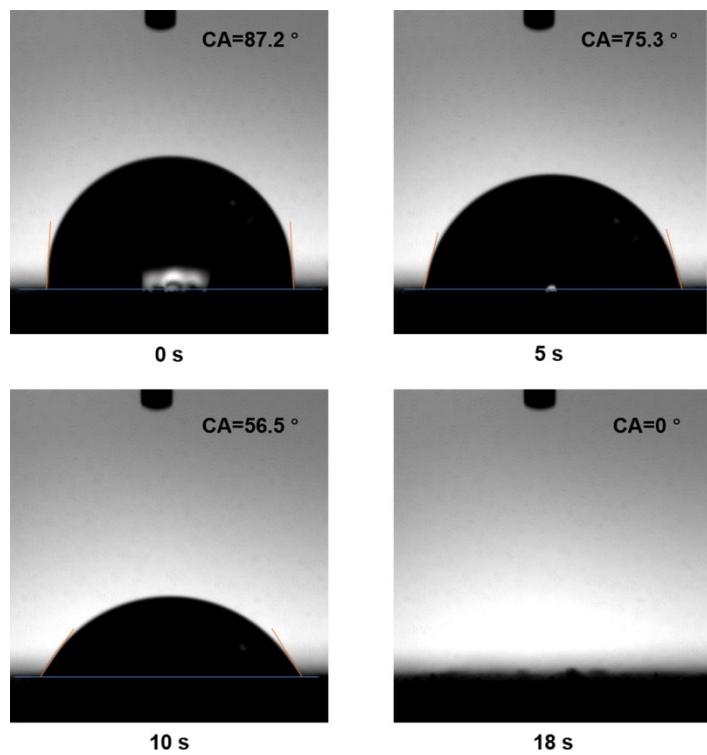


Figure S7. Droplet profiles with inserted static contact angle (CA) value (upper-right corner) on the β -CD@UiO-68-azo membrane surface at different measuring time.

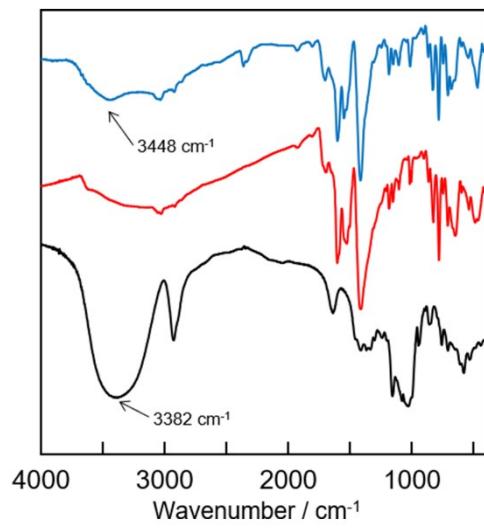


Figure S8. Anhydrous FTIR spectrums of β -CD (black), UiO-68-azo (red) and β -CD@UiO-68-azo (blue).

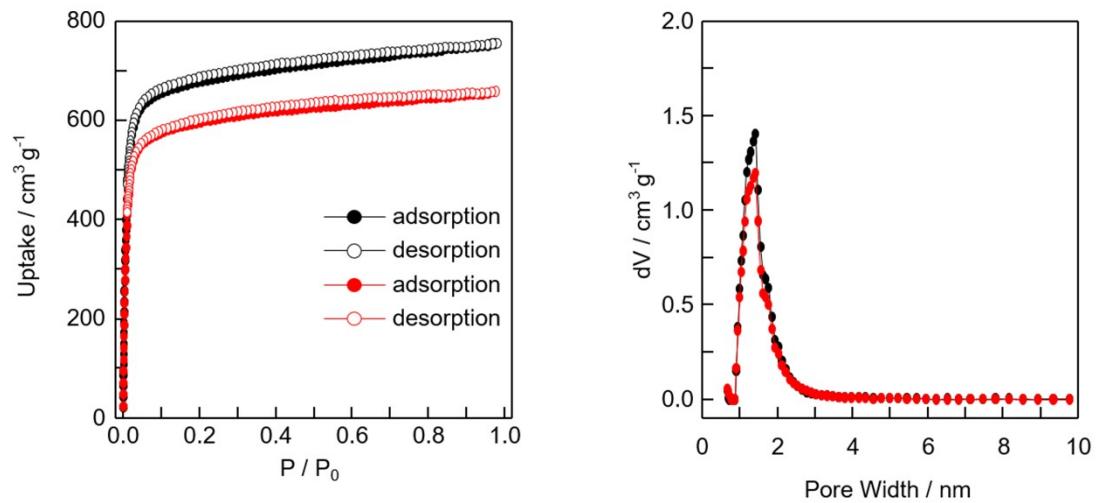


Figure S9. The N₂ sorption isotherm and pore size distribution of UiO-68-azo (black) and β -CD@UiO-68-azo (red). The BET surface area and pore size are 2629 m² g⁻¹, 2311 m² g⁻¹ and 1.41 nm, 1.41 nm respectively.

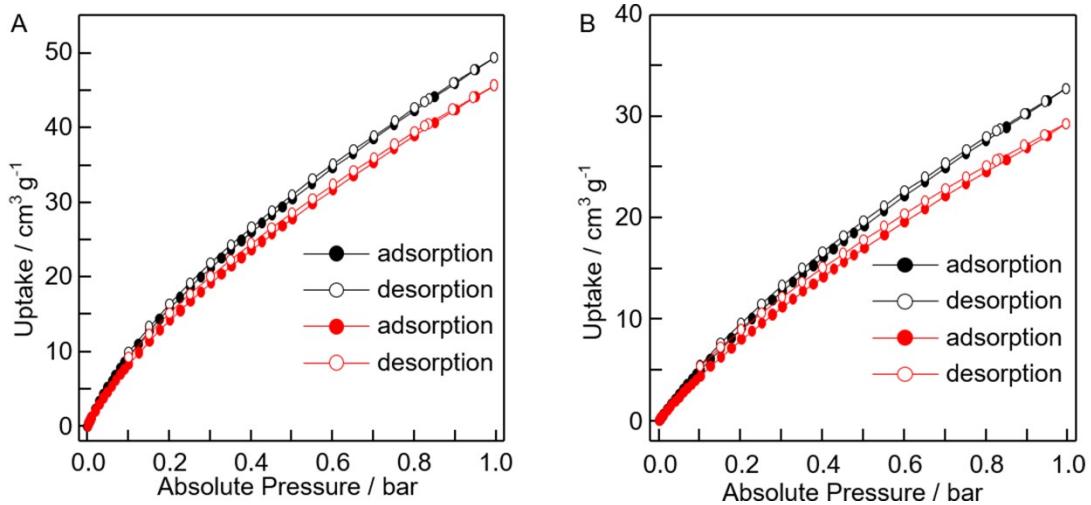


Figure S10. The CO₂ sorption isotherms of UiO-68-azo (black) and β-CD@UiO-68-azo (red) at A) 273 K and B) 298 K.

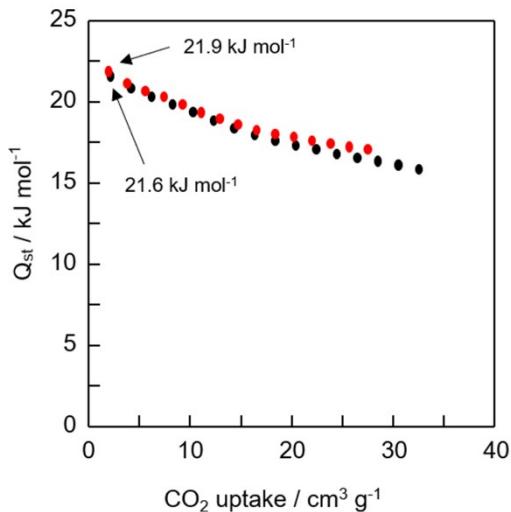


Figure S11. The isosteric enthalpy Q_{st} of CO₂ for UiO-68-azo (black) and β-CD@UiO-68-azo (red). The Q_{st} are 21.6 kJ mol⁻¹ and 21.9 kJ mol⁻¹ respectively.

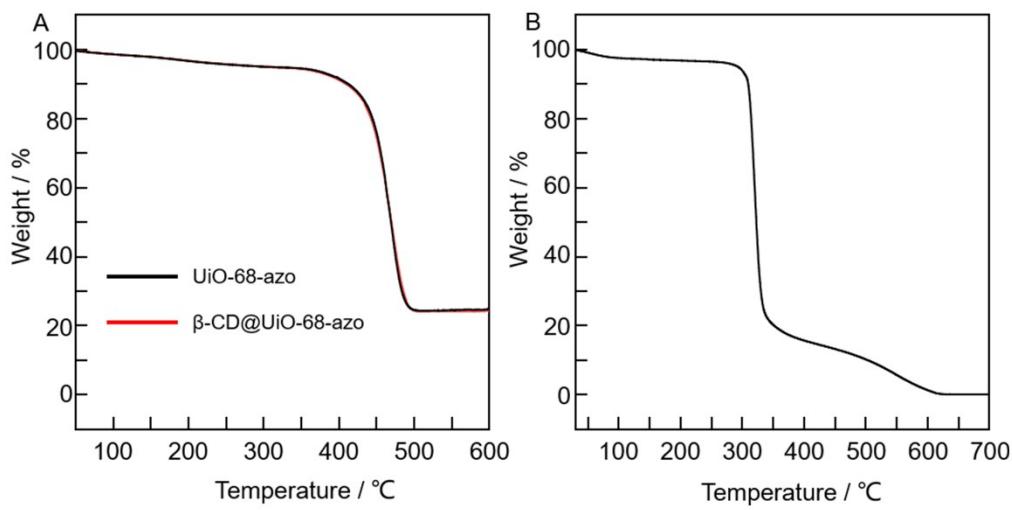


Figure S12. TGA curves of A) UiO-68-azo (black), β -CD@UiO-68-azo (red) and B) β -CD at atmosphere.

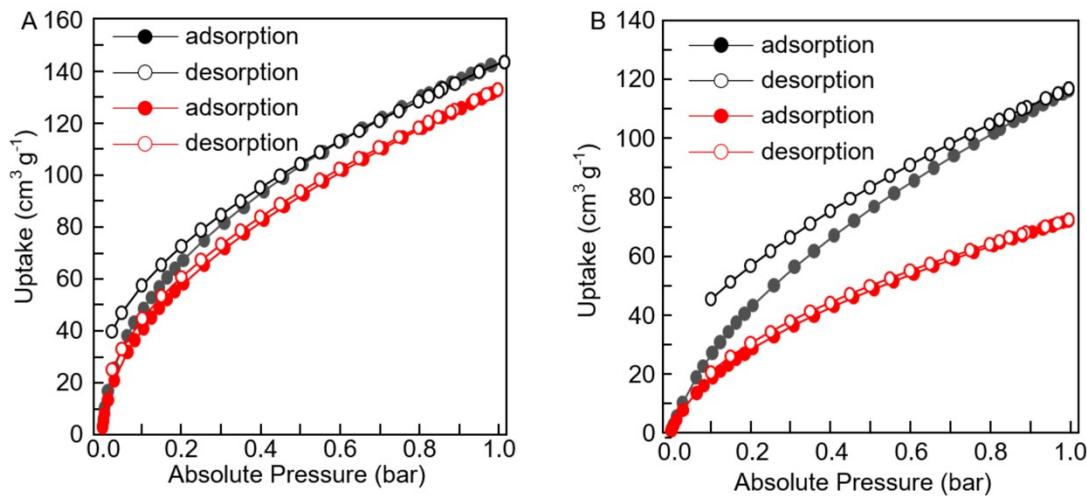


Figure S13. The H₂ adsorption of UiO-68-azo (black) and β -CD@UiO-68-azo (red) at A) 77 K and B) 87 K.

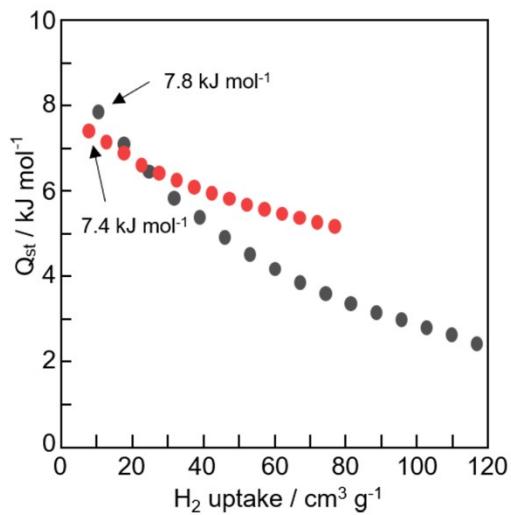


Figure S14. The H_2 Qst of UiO-68-azo (black) and $\beta\text{-CD@UiO-68-azo}$ (red). The Qst are 7.8 kJ mol^{-1} and 7.4 kJ mol^{-1} respectively.

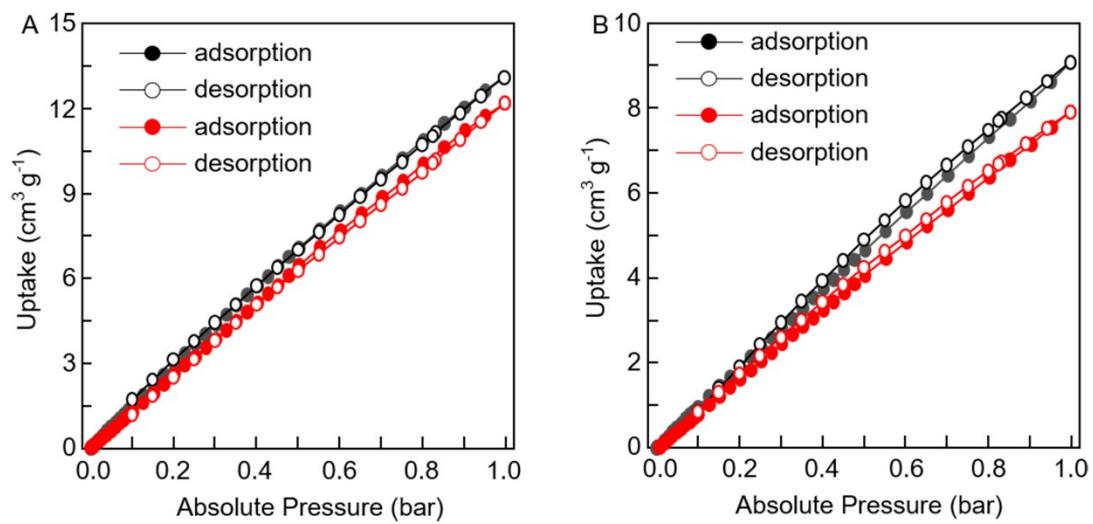


Figure S15. The CH_4 adsorption of UiO-68-azo (black) and $\beta\text{-CD@UiO-68-azo}$ (red) at A) 77 K and B) 87 K.

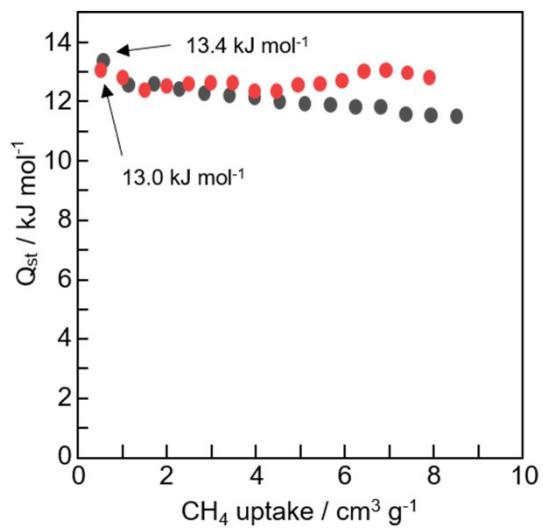


Figure S16. The CH_4 Q_{st} of UiO-68-azo (black) and $\beta\text{-CD@UiO-68-azo}$ (red). The Q_{st} are 13.4 kJ mol^{-1} and 13.0 kJ mol^{-1} respectively.

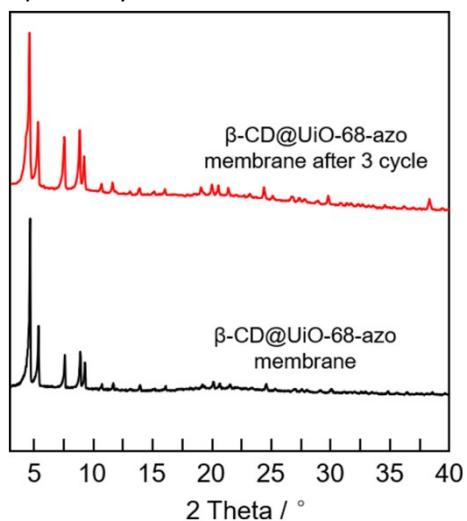


Figure S17. The XRD patterns of UiO-68-azo membrane (black) and $\beta\text{-CD@UiO-68-azo}$ membrane after 3 cycle of desorption/adsorption of $\beta\text{-CD}$ (red).

Table S1. H₂/CO₂ mixture gas separation performances of the UiO-68-azo membrane before and after UV irradiation at 1 bar and room temperature with 1:1 binary mixture.

Membrane	KC ^a	UiO-68-azo membrane			UiO-68-azo membrane after UV irradiation		
		P (i) ^b	P (j) ^b	SF ^c	P (i) ^b	P (j) ^b	SF ^c
1		131520	13152	14.9	121702	9447	17.9
2		132076	12596	15.4	121702	9261	18.0
3	4.7	145783	18523	13.5	144301	17968	14.6
4		130038	12967	16.5	121331	9076	18.6
5		143560	16671	16.1	142449	16486	17.2

^a. Knudsen constant. ^b. Permeability in Barrer. ^c. Separation factor.

Table S2. Mixture gas separation performances of the UiO-68-azo membrane and β-CD@UiO-68-azo membrane at 1 bar and room temperature with 1:1 binary mixture. (Membrane 1)

Gas _{i/j}	KC ^a	UiO-68-azo membrane			β-CD@UiO-68-azo membrane		
		P (i) ^b	P (j) ^b	SF ^c	P (i) ^b	P (j) ^b	SF ^c
H ₂ /CO ₂	4.7	130779	12781	15.0	107253	2778	46.6
H ₂ /N ₂	3.7	116145	14819	10.8	103919	5186	23.9
H ₂ /CH ₄	2.8	107253	23154	9.7	110958	9632	13.1

^a. Knudsen constant. ^b. Permeability in Barrer. ^c. Separation factor.

Table S3. Mixture gas separation performances of the UiO-68-azo membrane and β-CD@UiO-68-azo membrane at 1 bar and room temperature with 1:1 binary mixture. (Membrane 2)

Gas _{i/j}	KC ^a	UiO-68-azo membrane			β-CD@UiO-68-azo membrane		
		P (i) ^b	P (j) ^b	SF ^c	P (i) ^b	P (j) ^b	SF ^c
H ₂ /CO ₂	4.7	130038	12781	16.5	107809	2558	48.9
H ₂ /N ₂	3.7	119479	17227	9.3	102993	4797	21.9
H ₂ /CH ₄	2.8	130223	22414	7.8	110958	8314	12.9

^a. Knudsen constant. ^b. Permeability in Barrer. ^c. Separation factor.

Table S4. H₂/CO₂ Mixture gas separation performances of β-CD@UiO-68-azo membrane at 1 bar and different temperature (from 303 K to 323 K) with 1:1 binary mixture.

Temperature / °C	KC ^a	β-CD@UiO-68-azo membrane		
		P (i) ^b	P (j) ^b	SF ^c
30		102596	2957	44.8
40	4.7	108388	3455	41.1
50		118592	4964	32.5

^a. Knudsen constant. ^b. Permeability in Barrer. ^c. Separation factor.

Table S5. H₂/CO₂ Mixture gas separation performances of β-CD@UiO-68-azo membrane at room temperature and different pressure (feed gas pressure from 1bar to 1.4bar) with 1:1 binary mixture.

Pressure / bar	KC ^a	β-CD@UiO-68-azo membrane		
		P (i) ^b	P (j) ^b	SF ^c
1		99237	2686	47.3
1.1	4.7	97865	2864	42.4
1.4		80132	4931	20.3

^a. Knudsen constant. ^b. Permeability in Barrer. ^c. Separation factor.