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Electronic Supplementary Information for

Azo-bridged Covalent Porphyrinic Polymers (Azo-CPPs): Synthesis and CO₂ Capture

properties†

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Fig. S1 ¹H NMR spectrum of 4NO₂TPP (CDCl₃, 400 MHz)



Fig. S2 FT-IR spectrum of 4NO₂TPP (KBr pellets)



Fig. S3 Solid-state ¹³C NMR spectrum of 4NO₂TPP (100 MHz)



Fig. S4 FTIR spectra comparison of Azo-CPP-1 and the monomers (KBr pellets)



Fig. S5 FT-IR spectra of the Azo-CPPs. (KBr pellets)



Fig. S6 FT-IR spectra of the Azo-CPPs, expanded between $1800 \sim 1000 \text{ cm}^{-1}$. (KBr

pellets)



Fig. S7 TGA curves of Azo-CPPs. (N2, 10 °C /min)



Fig. S8 DSC curves of the Azo-CPPs. (10 °C/min, N₂)



Fig. S9 SEM images of Azo-CPP-1



Fig. S10 Nitrogen adsorption and desorption isotherms at 77.3 K for all Azo-CPPs.



Fig. S11 Pore size distributions (PSD) calculated by the NLDFT method for all Azo-CPPs.



Fig. S12 CO₂ adsorption isotherms at 273 K for all Azo-CPPs.



Fig. S13 Nitrogen adsorption and desorption isotherms at 77.3 K for Azo-CPP-1 and Azo-CPP-1-Pd.



Fig. S14 Pore size distributions (PSD) calculated by the NLDFT method for Azo-CPP-1 and Azo-CPP-1-Pd.



Fig. S 15 CO₂ adsorption isotherms at 273 K for Azo-CPP-1 and Azo-CPP-1-Pd



Fig. S16 CO₂/N₂ selectivities for Azo-CPP-1 calculated using the Henry's Law constants in the linear low pressure range (0~100 mbar).



Fig. S17 CO₂/N₂ selectivities for Azo-CPP-2 calculated using the Henry's Law constants in the linear low pressure range (0~100 mbar)



Fig. S18 CO_2/N_2 selectivities for Azo-CPP-3 calculated using the Henry's Law constants in the linear low pressure range (0~100 mbar). Due to the very low adsorption of N₂ at 303 K in the range of 0~100 mbar, the data from 150 to 500 mbar were used instead.



Fig. S19 CO_2/N_2 selectivities for Azo-CPP-4 calculated using the Henry's Law constants in the linear low pressure range (0~100 mbar). Due to the very low adsorption of N₂ at 303 K in the range of 0~100 mbar, the data from 90 to 500 mbar were used instead.



Fig. S20 CO_2/N_2 selectivities for Azo-CPP-5 calculated using the Henry's Law constants in the linear low pressure range (0~100 mbar). Due to the very low adsorption of N₂ at 303 K in the range of 0~100 mbar, the data from 100 to 500 mbar were used instead.





Fig. S21 CO_2/N_2 selectivities for Azo-CPP-6 calculated using the Henry's Law constants in the linear low pressure range (0~100 mbar). Due to the very low adsorption of N₂ at 303 K in the range of 0~100 mbar, the data from 100 to 500 mbar were used instead.



Fig. S22 CO_2/N_2 selectivities for Azo-CPP-7 calculated using the Henry's Law constants in the linear low pressure range (0~150 mbar).