Electronic Supplementary Information for

Network-controlled unique reactivities of carbonyl groups in hollow and microporous organic polymer

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Experimental Sections

Scanning electron (SEM) and transmission electron (TEM) microscopies were conducted using a FE-SEM (JSM6700F) and a JEOL 2100F unit, respectively. Elemental mapping TEM images were conducted based on the energy dispersive X-ray spectroscopy (EDS). N_2 and CO_2 adsorption behaviors of the MON materials were conducted using a BELSORP II-mini equipment. The pore size distribution diagrams were obtained based on the density functional theory (DFT) method. The temperature−programmed desorption (TPD) of CO_2 was carried out using a Micromeritics ASAP 2920 system installed with a thermal conductivity detector (TCD). Prior to the analysis, a 20 mg sample was loaded into a quartz tubular reactor and pretreated at 100°C under a He flow (30 mL/min) for 2 h. After cooling down to 10°C, CO_2 gas was passed through the sample bed at a flow rate of 30 mL/min for 0.5 h and then purged using He gas for 0.5 h at 10 °C to remove the weakly adsorbed CO_2. Finally, the CO_2 desorption profiles was recorded during the raising temperature from 10 °C to 300 °C at a ramp rate of 10 °C/min. Powder X-ray diffraction studies were conducted using a Rigaku MAX-2200 (filtered Cu-Ka radiation). The infrared absorption spectroscopy was conducted using a Bruker VERTEX 70 FT-IR spectrometer. Solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy was conducted in the CPTOSS mode using a 500 MHz Bruker ADVANCE II NMR spectrometer at the NCIRF of Seoul National University. A 4 mm magic angle spinning probe was used. The spinning rate was 5 kHz. Solution based NMR studies were conducted using a 400 MHz and 500 MHz Varian spectrometers. Elemental analysis was conducted using a CE EA1110 instrument. The computational simulation was conducted based on the density functional theory (DFT) with ωB97X-D/6-311+G(d,p) level which can describe dispersion energy.[1] (Refer to Fig. S3 in the ESI)

Synthetic procedure for H-MON-CO

Silica spheres with an average size of 397 nm were prepared by the synthetic method reported in the literature.[2] In our work, the following procedures were applied. In a 250 nm round bottomed flask, ethanol (200 mL), distilled water (23.5 mL), ammonium hydroxide solution (28~30%, 7 mL) were added. The mixture was stirred at 1150 rpm for 5 mins. After tetraethyl orthosilicate (17.5 mL) was added, the reaction mixture was stirred at 1150

rpm for 18 hours at room temperature. The silica spheres were separated by centrifugation, washed with ethanol and hexane, and dried under vacuum. The amount of isolated silica spheres was ~3.5 g. Tetrakis(4-ethynylphenyl)adamantane was prepared by the synthetic method reported in the literature.[3] In a flame-dried 50 mL Schlenk flask, silica sphere (0.30 g), $(PPh_3)_2PdCl_2$ (8.4 mg, 0.012 mmol), and CuI (2.3 mg, 0.012 mmol) were added. After triethylamine (15 mL) and toluene (15 mL) were added, the reaction mixture was sonicated for 2 hours. After tetrakis(4-ethynylphenyl)adamantane (64 mg, 0.12 mmol) and 1,4-diiodobenzene (79 mg, 0.24 mmol) were added, the reaction mixture was bubbled with CO gas for 1 min. The reaction mixture was heated at 80°C for 48 hours under CO (balloon). After the mixture being cooled to room temperature, the SiO_2@MON-CO was separated by centrifugation, washed with methanol, methylene chloride, acetone, and then methanol again (three times each), The isolated SiO_2@MON-CO was added to a 50 mL Falcon tube. A mixture of HF (48~51% aqueous solution, 5 mL), water (25 mL), and methanol (20 mL) was added. *Caution: The HF is an extremely toxic and thus, should be handled with specific gloves in a hood.* The reaction mixture was stirred for 2 hours at room temperature. H-MON-CO was separated by centrifugation, washed with a 1:1 mixture of methanol and water five times, acetone three times, and dried under vacuum. The amount of isolated H-MON-CO was ~80 mg. Elemental analysis of H-MON-CO showed 80.41, 5.04, 0.99, and 6.06% contents for carbon, hydrogen, nitrogen, and oxygen, respectively.

Synthetic procedures for H-MON-HZ and reaction procedures of H-MON-CO with nucleophiles

In a flame dried 50 mL Schlenk flask, H-MON-CO (50 mg, 0.19 mmol carbonyl moiety, 3.79 mmol carbonyl/g based on the elemental analysis) and distilled toluene (15 mL) were added under argon. After hydrazine monohydrate (0.12 mL, 2.4 mmol) was added, the reaction mixture was heated at 80°C for 24 hours under argon. The reaction progress can be checked by IR studies (refer to the text). After the reaction mixture being cooled to room temperature, the H-MON-HZ was separated by centrifugation, washed with methanol, methylene chloride, and acetone (three times each), and dried under vacuum. The amount of isolated H-MON-HZ was ~40 mg. Elemental analysis of H-MON-HZ showed 76.79, 5.17, 8.39, and 2.79% contents for carbon, hydrogen, nitrogen, and oxygen, respectively.

For the reaction of n-BuLi or MeLi with H-MON-CO, the H-MON-CO (30 mg, 0.12 mmol of carbonyl group, 3.79 mmol carbonyl/g based on elemental analysis) was dispersed in diethyl ether (20 mL). n-BuLi or MeLi (1.6 M in hexane, 0.91 mL, 1.5 mmol) was slowly added to the reaction mixture at -78°C. The reaction mixture was stirred at -78°C for 12 hours. When the reaction mixture was stirred at room temperature for 12 hours, the obtained IR spectrum was nearly same as that of the reaction at -78°C. The reaction mixture was quenched by addition methanol. The solid powder was separated by centrifugation, washed with methanol, methylene chloride, and acetone (three times each), and dried under vacuum. The reaction progress was checked by IR studies.

For the reaction of $LiAlH_4$ with H-MON-CO, the H-MON-CO (30 mg, 0.12 mmol of carbonyl group, 3.79 mmol carbonyl/g based on elemental analysis) was dispersed in diethyl ether (20 mL). $LiAlH_4$ (55 mg, 1.5 mmol) was added to reaction mixture at 0°C. After being stirred at room temperature for additional 12 hours, the reaction

mixture was quenched by adding methanol. When the reaction mixture was refluxed for 12 hours, the obtained IR spectrum was nearly same as that of the reaction at room temperature. The solid powder was separated by centrifugation, washed with methanol, methylene chloride, and acetone (three times each), and dried under vacuum. The reaction progress was checked by IR studies described in text.

Experimental procedures for molecular model reactions

The formation of the model alkynone compound, 1,3-diphenyl-2-propynone was confirmed in the reaction of phenylacetylene and iodobenzene under the same synthetic conditions used for H-MON-CO. In a flame-dried 250 Schlenk flask, $(PPh_3)_2PdCl_2$ (84 mg, 0.12 mmol), CuI (23 mg, 0.12 mmol), triethylamine (50 mL), and toluene (50 mL) were added. After phenylacetylene (0.13 mL, 1.2 mmol) and iodobenzene (0.13 mL, 1.2 mmol) were added, the reaction mixture was bubbled with CO for 1 min. The reaction mixture was heated at 80°C for 48 hours under CO (balloon). After the mixture being cooled to room temperature, the volatile reagents were removed by a rotary evaporator. The product was extracted using chloroform and water. After the chloroform solution was dried by $MgSO_4$, the solvent was removed by a rotary evaporator. The 1,3-diphenyl-2-proynone was separated by flash column chromatography using a 9:1 mixture of hexane and methylene chloride as an eluent. Isolated yield was 28.1%. The ^1H and ^{13}C NMR spectra of the product matched well with those in the literature.[4] ^1H NMR of product: (500 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.2, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR of product: (125MHz, $CDCl_3$): δ = 178.1, 136.9, 134.1, 133.1, 130.8, 129.6, 128.7, 128.7, 120.2, 93.1, 86.9 ppm. HR-MS for $C_{15}H_{10}O$, FAB mode, $[M+H]^+$ calcd, 207.0810, found, 207.0808.

In a flame dried 50 mL Schlenk flask, 1,3-diphenyl-2-propynone (0.17 g, 0.81 mmol) was dissolved in distilled diethyl ether (20 mL) under argon. n-Butyllithium (1.6 M in hexane, 5.1 mL, 8.1 mmol) was slowly added at -78°C. The reaction mixture was stirred at -78°C for 12 hours. After the mixture being quenched with methanol and being cooled to room temperature, the volatile solvent was removed by a rotary evaporator. The mixture was dissolved in methylene chloride and loaded on the flash silica column chromatography. The product (n-butyl adduct to 1,3-diphenyl-2-propynone) was separated using a 10:1 mixture of hexane and ethyl acetate. Isolated yield was 94.4 %. The ^1H and ^{13}C NMR spectra of the product matched well with those in the literature.[5] ^1H NMR of product: (500 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.3 Hz, 2H), 7.48 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 1H), 2.56 (s, 1H), 2.12 – 1.87 (m, 2H), 1.60 – 1.25 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR of product: (125MHz, $CDCl_3$): δ = 144.9, 131.8, 128.5, 128.4, 128.2, 127.7, 125.6, 122.7, 122.7, 91.7, 86.1, 77.4, 77.1, 76.9, 73.8, 45.3, 27.0, 22.8, 14.1 ppm. HR-MS for $C_{19}H_{20}O$, EI mode, calcd, 224.1514, found, 244.1511.

For the reaction of MeLi addition to 1,3-diphenyl-2-propynone, the same procedures applied for the synthesis of n-butyl adduct to 1,3-diphenyl-2-propynone were used except using MeLi (1.6 M in hexane, 4.7 mL, 7.5 mmol) and 1,3-pdiphenyl-2-propynone (0.15 g, 0.75 mmol). Isolated yield was 96.1%. The ^1H and ^{13}C NMR spectra of the product matched well with those in the literature.[6] ^1H NMR of product: (500 MHz, $CDCl_3$): δ = 7.73 (d, *J* =

7.4 Hz, 2H), 7.48 (m, 2H), 7.39 (t, *J* = 7.1 Hz, 2H), 7.36 – 7.27 (m, 4H), 2.49 (s, 1H), 1.87 (s, 3H) ppm. ^{13}C NMR of product: (125MHz, $CDCl_3$): δ = 145.7, 131.8, 128.5, 128.4, 128.3, 127.8, 125.0, 122.6, 92.5, 85.0, 70.4, 33.3 ppm. HR-MS for $C_{16}H_{14}O$, EI mode, calcd, 222.1045, found, 222.1040.

For the reaction of $LiAlH_4$ addition to 1,3-diphenyl-2-propynone, the 1,3-diphenyl-2-propynone (0.16 g, 0.78 mmol) was dissolved in a distilled diethyl ether (20 mL). $LiAlH_4$ (0.29 g, 7.8 mmol) was added to reaction mixture at 0^{o}C. After the reaction mixture was stirred at 0^{o}C for 30 min, the reaction mixture was further stirred at room temperature for 12 hours. After the reaction mixture was quenched with methanol, the solvent was removed by a rotary evaporator. The mixture was dissolved in methylene chloride and filtered through a Celite powder. The product was separated by the flash silica column chromatography using a 10:1 mixture of hexane and ethyl acetate. Isolated yield was 90.8%. The ^{1}H and ^{13}C NMR spectra of the product matched well with those in the literature.[7] ^{1}H NMR of product: (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.38 (dd, *J* = 15.8, 6.5 Hz, 1H), 5.38 (d, *J* = 6.5 Hz, 1H), 2.06 (s, 1H) ppm. ^{13}C NMR of product: (125MHz, $CDCl_3$): δ = 142.8, 136.5, 131.5, 130.6, 128.7, 128.6, 127.8, 127.8, 126.6, 126.4, 75.2 ppm. HR-MS for $C_{15}H_{14}O$, EI mode, calcd, 210.1045, found, 210.1045.

For the reaction of hydrazine with 1,3-diphenyl-2-propynone, the 1,3-diphenyl-2-propynone (0.20 g, 0.95 mmol) was dissolved in distilled toluene (20 mL) in a 50 mL Schlenk flask under argon. After hydrazine monohydrate (0.46 mL, 9.5 mmol) was added, the reaction mixture was heated at 80^{o}C for 24 hours. After the reaction mixture being cooled to room temperature, the solvent was evaporated. The mixture was extracted using methylene chloride and water. After the mixture solution was dried using $MgSO_4$, the solvent was removed by a rotary evaporator. Without further purification, the pure product (3,5-diphenylpyrazole) was obtained. Isolated yield was 98.3%. The ^{1}H and ^{13}C NMR spectra of the product matched well with those in the literature.[8] ^{1}H NMR of product: (500 MHz, $CDCl_3$): δ =10.67 (s, 1H), 7.74 (d, *J* = 7.2 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 6.86 (s, 1H) ppm. ^{13}C NMR of product: (125MHz, $CDCl_3$): δ = 127.9, 127.3, 124.6, 99.2 ppm. HR-MS for $C_{15}H_{12}N_2$, EI mode, calcd, 220.1000, found, 220.1002.

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Fig. S1 IR spectra of MON prepared by the Sonogashira coupling of tetrakis(4-ethynylphenyl)adamantane with 1,4-diiodobenzene without CO, model alkynone compound, and H-MON-CO.

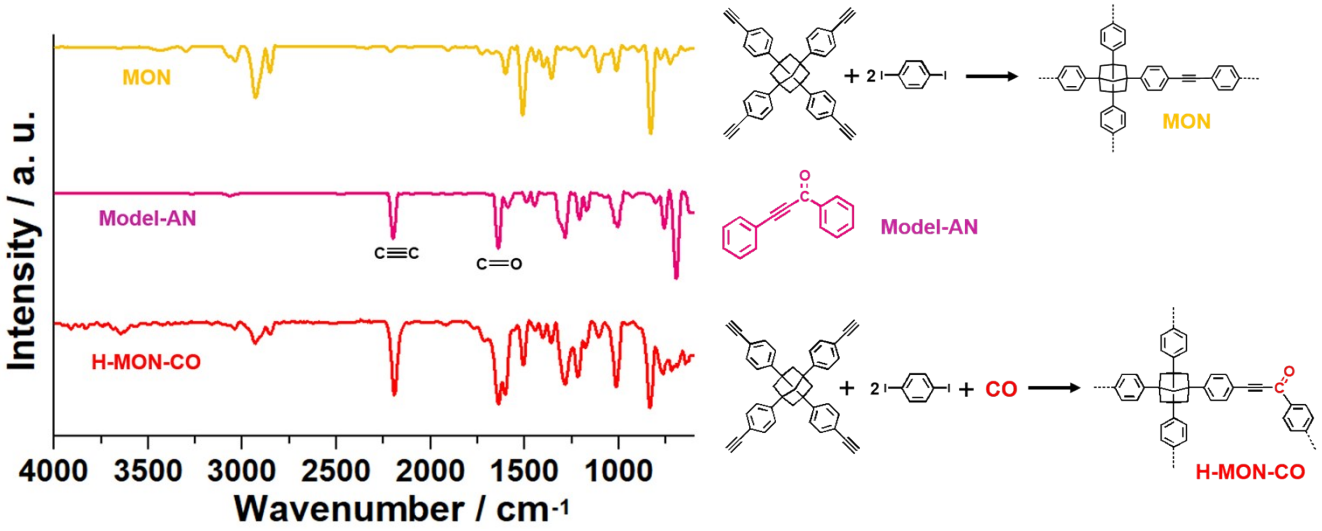


Fig. S2 PXRD pattern of H-MON-CO and H-MON-CO.

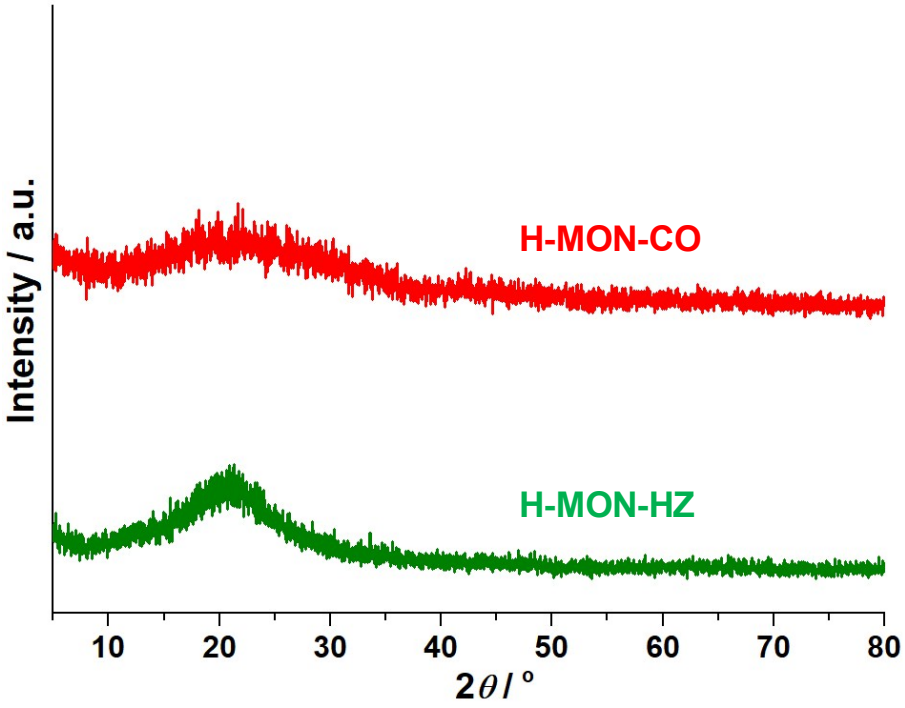
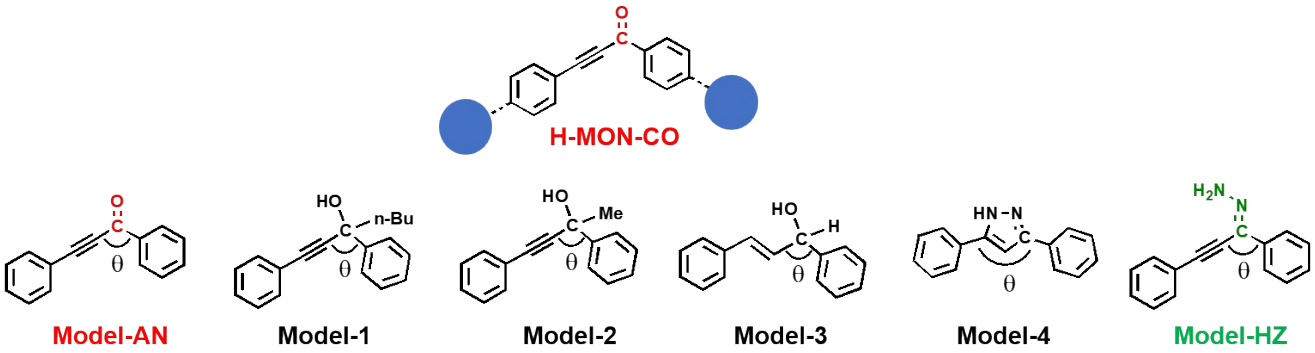


Fig. S3 Computational simulation of the expected strain energies resulted from the chemical conversions of alkynone moieties in the network maintaining the original bent angle (θ, 117.2°).[a]



Compounds	Model-AN	Model-1	Model-2	Model-3	Model-4	Model-HZ
Optimized Angles and Angle Differences[b] (θ and |Δθ| in °)	117.2 (0.00)	109.4 (7.8)	111.0 (6.2)	110.6 (6.6)	152.3 (35.1)	119.5 (2.3)
Expected Strain Energy[c] : Energy differences between the fully optimized structure and the optimized structures with a fixed θ as 117.2 ° (ΔE in kJ/mol)	0.00	12.93	6.36	6.15	101.92	1.00[c]

[a] To shed light on the reason behind the results of post-synthetic modification of H-MON-CO, we carried out density functional theory (DFT) calculations with a *ω*B97X-D/6-311+G(d,p) level which can describe dispersion energy. The calculated angles (θ in Figure above) of optimized structure for model compounds were listed. The optimized θ for MON-AN is calculated to be 117.2 °. It is also shown that the Model-1~4 have an absolute deviation of θ (|Δθ|) with respect to that of MON-AN in the range of 6.2 ~ 35.1 °. It is noticeable that the smallest |Δθ| value (2.3 °) is found in Model-HZ. Next, we tried to calculate the molecular energy differences (ΔE in kJ/mol) between the fully optimized structure and the optimized structure with a fixed angle as the optimized θ of Model-AN (117.2°) for Model-HZ and Model-1~4. If we assume that the Model-AN moieties in H-MON-CO would have a restriction of θ changes owing to structural rigidity in network systems, the calculated ΔEs for Model 1~4 and MON-HZ could represent a part of extra energy requirement to complete the reactions beyond structural rigidity. We found that the calculated |Δθ| and ΔE have roughly same ascending order of their magnitudes between Model-1~4 and Model-HZ. Interestingly, only Model-HZ shows the calculated ΔE, that is, 1.00 kJ/mol lower than the room temperature energy (2.47 kcal/mol). This might be the main reason for the observation of Model-HZ moieties rather than Model-4 in the post-synthetic modification of H-MON-CO.

[b] The difference between the optimized bent angle (117.2°) of Model-AN and other compounds.

[c] It is noteworthy that the room temperature energy is 2.47 kJ/mol. The expected strain energy for Model-HZ (1.00 kJ/mol) is lower than the room temperature energy.

Fig. S4 Comparison of IR spectra of H-MON-HZ with model compounds.

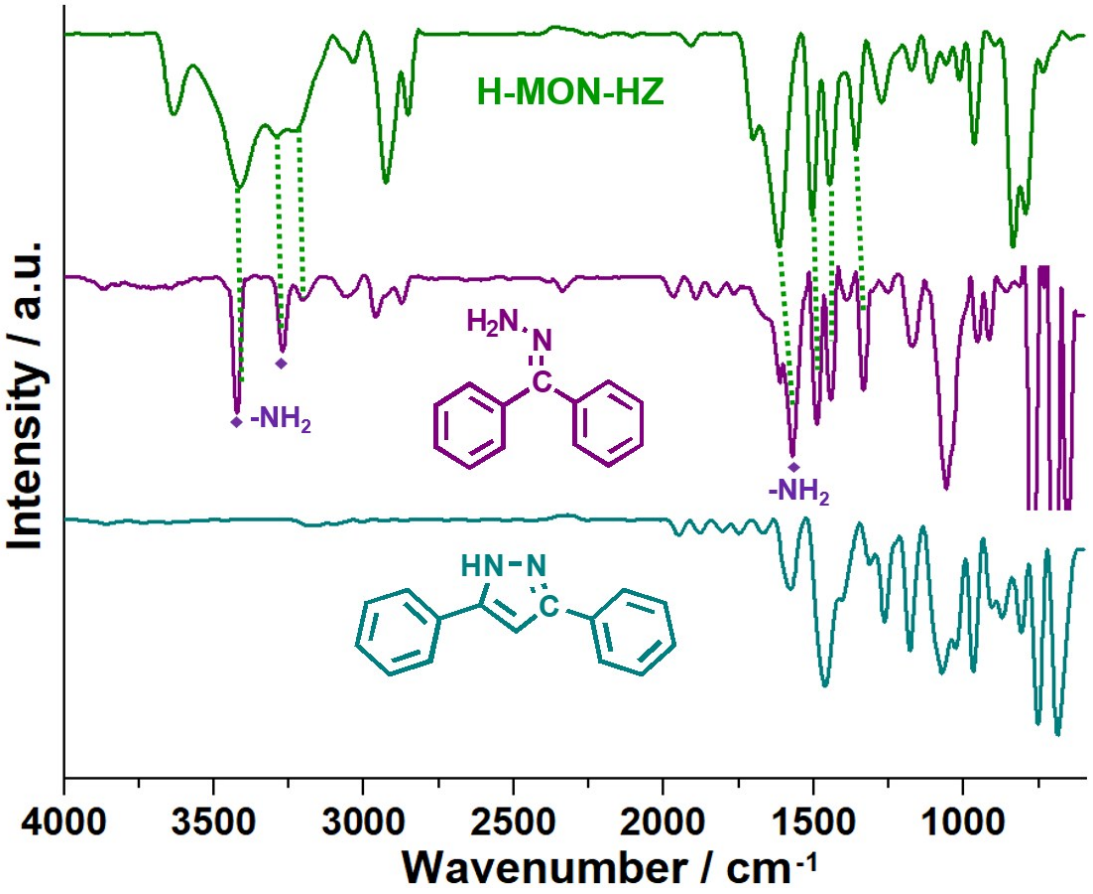


Fig. S5 CO_2 adsorption/desorption behaviors of H-MON-HZ at 195K.