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Room-Temperature Synthesis of a Hollow Microporous Organic Polymer Bearing Activated Alkyne IR Probes for Nonradical Thiol-yne Click-Based Post-Functionalization

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Abstract: This work shows that hollow microporous organic polymer (H-MOP-A) with activated internal alkynes as IR probes can be prepared by template synthesis based on acyl Sonogashira-Hagihara coupling at room temperature. The H-MOP-A is a versatile platform in the main chain PSM based on nonradical thiol-yne click reaction. Moreover, an IR peak of internal alkynes in the H-MOP-A is very intense and could be utilized in the monitoring of thiol-yne click-based main chain PSM. The functionalized H-MOP-A with carboxylic acids (H-MOP-CA) showed efficient adsorption toward Ag^+ ions. The resultant H-MOP-CA-Ag showed excellent performance in the CO_2 fixation to α-alkylidene cyclic compounds.

Since Cooper *et al.* first reported that conjugated microporous polymers (CMPs) can be prepared by the Sonogashira-Hagihara coupling of aryl alkynes and aryl halides,[1] there have been extensive studies on the development of functional CMPs.[2] Weber *et al.* reported that tailored functionality can be further incorporated into main chain networks of CMP through post-synthetic modification (PSM), based on radical-induced thiol-yne click chemistry.[3] Since the pioneering report of Weber *et al.*, various functional CMPs have been prepared by the thiol-yne click reaction and applied as adsorbents and catalysts.[4]

According to our previous studies, thiols were added to defect sites of CMPs through radical-induced thiol-yne reaction.[5] Compared with molecular click chemistry, the reactivity of internal alkynes in the main chain networks of CMP can be suppressed by a network-induced geometrical constraint.[6] In the solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, most internal alkynes in the main chain networks of CMPs were actually intact in the radical-induced thiol-yne click reaction.[5] The amount of incorporated thiols in CMPs is limited to their defective degree.

The radical-induced thiol-yne reaction is powerful in the incorporation of thiols into alkynes and is called the "click reaction".[7] In comparison, nonradical thiol addition to internal alkynes is relatively less efficient. In addition, thiols with potentially radical quenching moieties can be inefficient in the radical-induced thiol-yne reaction. If the chemical reactivities of internal alkynes can be enhanced, thiols can be added without the help of radical species. Thus, more exploration is required for CMP and CMP-like materials with activated alkynes.

The vibrations of internal alkynes with symmetric aryl substituents are known to be very weak in infrared (IR) response.[8] The IR vibration peaks of internal alkynes in the CMP are known to appear at ~2200 cm^{-1} with very weak intensity.[8] Thus, the IR monitoring of thiol-yne-based main chain PSM of CMP is inefficient. If chemical substituents of internal alkynes are not symmetric, IR spectroscopy can be a good tool in the monitoring of thiol-yne-based main chain PSM of CMP.

While the conventional Sonogashira-Hagihara coupling of aryl alkynes with aryl halides results in diaryl alkynes, so-called acyl Sonogashira-Hagihara coupling of aryl alkynes with acyl halides produces arylbenzoyl alkynes.[9] Compared with the diaryl alkynes, arylbenzoyl alkynes have IR-active alkyne moieties with asymmetric substituents. Moreover, while conventional Sonogashira-Hagihara coupling is conducted at high temperature, acyl Sonogashira-Hagihara coupling can be conducted at room temperature. In addition, microporous organic polymers (MOPs) can be prepared by carbonylative and acyl Sonogashira-Hagihara coupling.[10]

Recently, various hollow catalysts have been engineered by a template method, showing enhanced performance, due to the efficient utilization of catalytic sites and the reduced diffusion pathways of substrates.[11] In this work, we report the template synthesis of hollow microporous organic polymer (H-

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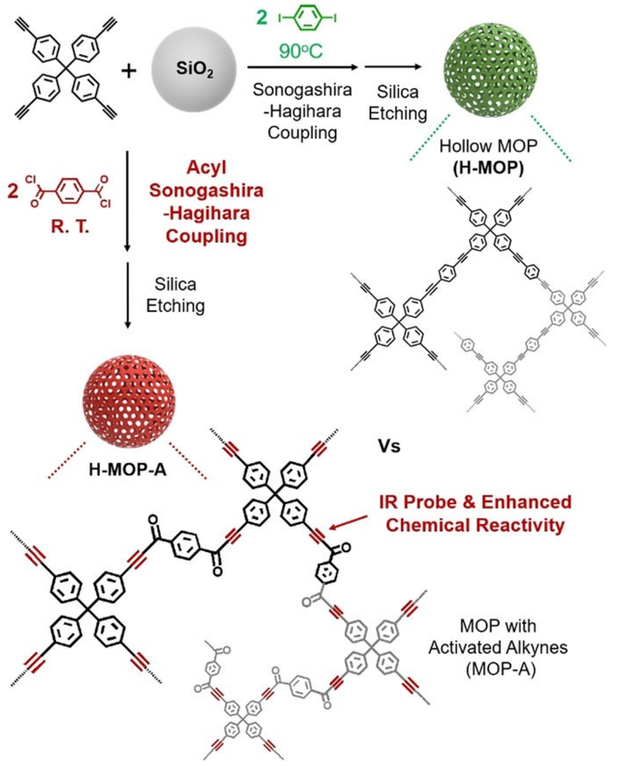

Figure 1. Template synthesis of H-MOP-A and H-MOP based on the acyl Sonogashira-Hagihara coupling and conventional Sonogashira-Hagihara coupling, respectively.

MOP) by the acyl Sonogashira-Hagihara coupling at room temperature and IR-monitorable PSM based on nonradical thiol-yne reactions. We use the term, MOP instead of CMP because the materials in this work are not fully conjugated.

Figure 1 shows a synthetic scheme for acyl Sonogashira-Hagihara coupling-based hollow MOP (H-MOP-A) using silica spheres with a diameter of 240 nm as templates.

The reaction was conducted at room temperature using 1 eq. tetra(4-ethynylphenyl)methane[12] and 2 eq. 1,4-terephthaloyl chloride as building blocks. The homogeneous coating of MOP on the silica templates was characterized by scanning (SEM) and transmission electron microscopy (TEM) and infrared absorption (IR) spectroscopy (Figure S1 in the SI). The silica etching from SiO$_2$@MOP-A through the treatment with HF solution resulted in the H-MOP-A. As a control material, conventional Sonogashira-Hagihara coupling-based hollow MOP (H-MOP) was prepared at 90 °C using 1 eq. tetra(4-ethynylphenyl)methane, 2 eq. 1,4-diiodobenzene, and silica templates, referring to the literature methods.[13]

SEM studies showed the homogeneous hollow morphologies of H-MOP-A and H-MOP with average diameters of 305 and 290 nm, respectively (Figure 2a–b and 2d–e). According to TEM analysis, the hollow structures with homogeneous shells of H-MOP-A and H-MOP were confirmed. The average shell thicknesses of H-MOP-A and H-MOP were measured to be 32 and 25 nm, respectively (Figure 2c and 2f). Analysis of the N$_2$ adsorption-desorption isotherm curves based on the Brunauer-Emmett-Teller (BET) theory indicated that the H-MOP-A and H-MOP have surface areas of 346 and 490 m^2/g, respectively (Figure S2 in the SI). The analysis of pore size distribution based on the density functional theory (DFT) method revealed that both H-MOP-A and H-MOP are microporous with main pore sizes of <2 nm (Figure S2 in the SI).

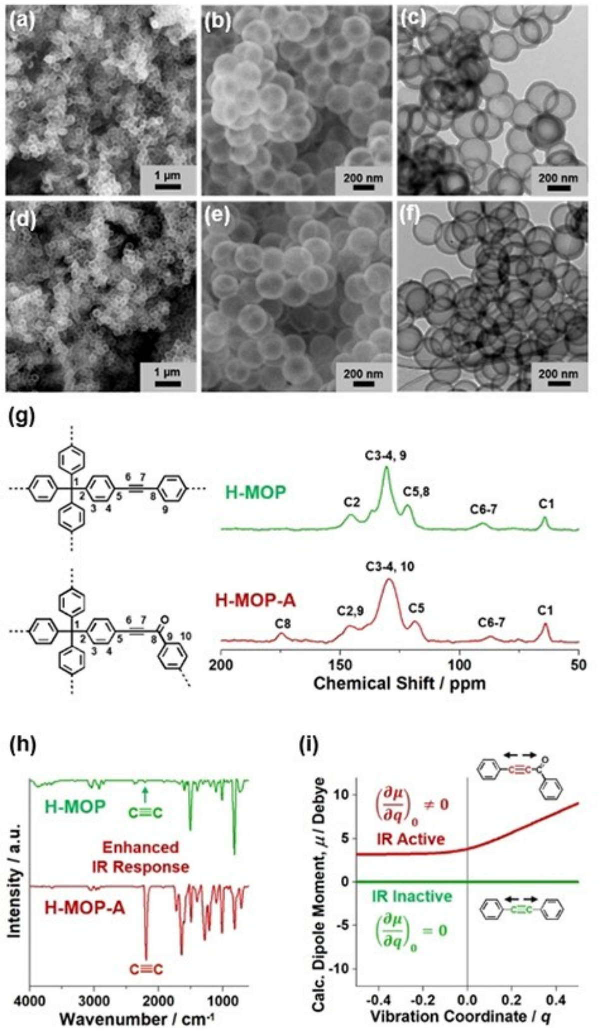

Figure 2. SEM images of (a–b) H-MOP-A and (d–e) H-MOP. TEM images of (c) H-MOP-A and (f) H-MOP. (g) Solid state ^{13}C NMR (CP/TOSS) and (h) IR absorption spectra of H-MOP and H-MOP-A. (i) Simulation of the dipole moment changes of 1,3-diphenylpropynone and 1,2-diphenylacetylene depending on vibration coordinates.

The solid state ^{13}C nuclear magnetic resonance (NMR) spectrum of H-MOP showed aromatic ^{13}C peaks at 122, 131, 137, and 146 ppm (Figure 2g). The ^{13}C peaks of internal alkynes and benzyl carbons appeared at 90 and 64 ppm, respectively, indicating that the H-MOP was formed through the Sonogashira-Hagihara coupling of the building blocks. Similarly, the solid state ^{13}C NMR spectrum of H-MOP-A showed aromatic ^{13}C peaks at 119, 129, 138, and 145 ppm (Figure 2g). The ^{13}C peaks of internal alkynes and benzyl carbons appeared at 87 and 64 ppm, respectively. In addition, the carbonyl ^{13}C peak was clearly observed at 175 ppm, indicating that the propynone moieties were incorporated into the chemical structure of H-

CMP-A through the acyl Sonogashira-Hagihara coupling of the building blocks.

The IR spectrum of H-MOP revealed main peaks at 1507 and 824 cm^{-1}, corresponding to aromatic C=C and C–H vibrations, respectively (Figure 2h). While the peak of internal alkynes in H-MOP was observed at 2212 cm^{-1}, its intensity was very weak. In comparison, the IR spectrum of H-MOP-A showed a very sharp peak of internal alkynes at 2194 cm^{-1} with very strong intensity, in addition to a carbonyl peak at 1644 cm^{-1}. The dramatically different IR responses of the internal alkyne moieties of H-MOP-A and H-MOP were rationalized by computational simulation (Figure 2i and S3 in the SI). Because 1,3-diphenylpropynone, a model compound of H-MOP-A, has asymmetric chemical substituents on internal alkynes, the symmetric stretching of the internal alkynes results in big changes of dipole moment. In comparison, 1,2-diphenylacetylene, a model compound of H-MOP, showed no changes of dipole moment with symmetric stretching of internal alkynes, resulting in an inactive IR response. Whilst the combustion elemental analysis revealed that the H-MOP and H-MOP-A are defective materials (Table S1 in the SI), the C–H vibration peaks of terminal alkynes were not observed at 3250~3300 cm^{-1} in their IR spectra (Figure 2h).

The benefits of H-MOP-A were explored in the thiol-yne click-based PSM. First, 3-mercaptopropionic acid was added to H-MOP through nonradical thiol-yne reaction, resulting in H-MOP-1 (Figure 3). Second, H-MOP was treated with 3-mercaptopropionic acid in the presence of azobisisobutyronitrile (AIBN) to form H-MOP-2. Whilst elemental analysis of the H-MOP-1 showed no detection of sulfur, the H-MOP-2 showed sulfur content of 0.87 wt% (Table S1 in the SI). These observations indicate that the nonradical thiol-yne reaction is inefficient for the PSM of H-MOP. In addition, the relatively poor PSM degree of H-MOP-2 is attributable to the possible radical quenching by carboxylic groups and the suppressed reactivities of internal alkynes in the network.

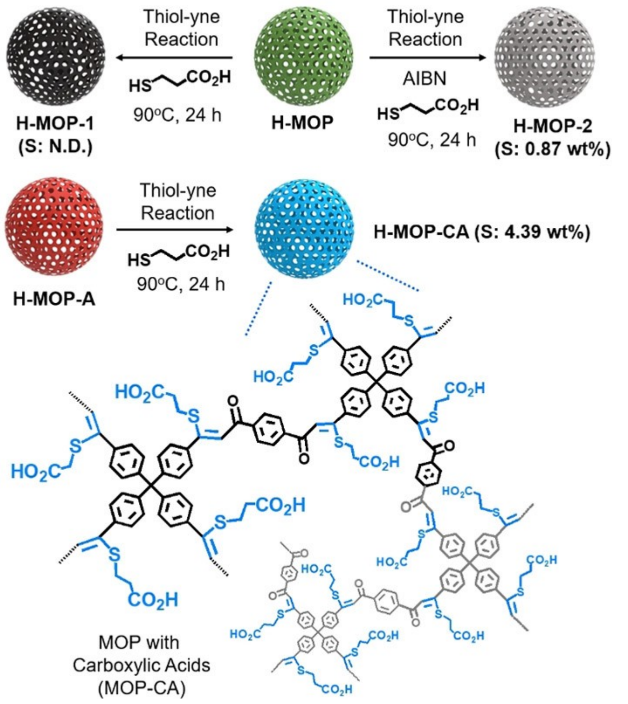

Figure 3. PSM of H-MOP and H-MOP-A based on radical and nonradical thiol-yne reactions with 3-mercaptopropionic acid.

In comparison, when H-MOP-A was treated with 3-mercaptopropinic acid without AIBN, the resultant H-MOP-CA showed a sulfur content of 4.39 wt%, corresponding to 1.37 mmol $SC_2H_4CO_2H$ per g (Table S1 in the SI).

The reactivities of H-MOP and H-MOP-A towards 3-mercaptopropionic acid were rationalized by molecular model studies (Figure 4). First, a model compound of H-MOP-A, 1,3-diphenylpropynone showed excellent reactivity in the nonradical thiol-yne reaction of 3-mercaptopropionic acid, resulting in thiol adducts with a 90% yield without the help of AIBN.[14] In sharp contrast, 1,2-diphenylacetylene showed completely no reactivity in the nonradical thiol-yne reaction with 3-mercaptopropionic acid. With the help of AIBN, the 1,2-diphenylacetylene and 3-mercaptopropionic acid showed thiol adducts with a relatively poor yield of 33%, possibly due to the radical quenching by carboxylic groups.[15] These model studies indicate that the H-MOP-A is beneficial over H-MOP in the thiol-yne click-based PSM with 3-mercaptopropionic acid.

SEM analysis showed that the H-MOP-CA, H-MOP-1, and H-MOP-2 retained the original hollow morphologies of H-MOP-A and H-MOP (Figure 5a–c). The PSM of H-MOP and H-MOP-A was investigated by IR and solid state ^{13}C NMR spectroscopies (Figure 5d-e). In the PSM of H-MOP to H-MOP-1 and H-MOP-2, there were no significant changes in IR and solid state ^{13}C NMR spectra. In comparison, the strong IR peak of internal alkynes at 2194 cm^{-1} disappeared in the IR spectrum of H-MOP-CA with appearance of new peaks (C=O: 1717 cm^{-1}, O–H: 3470 cm^{-1}, aliphatic C–H: 2960 cm^{-1}) of propionic acid groups, indicating the original internal alkyne IR peak at 2194 cm^{-1} can be utilized as an IR probe for the monitoring of thiol-yne click-based PSM.

In the ^{13}C NMR spectra, while the original carbonyl peak shifted from 175 ppm to 191 ppm through the PSM of H-MOP-A to H-MOP-CA, the peak of internal alkyne in H-MOP disappeared. In addition, new peaks of propionic acid groups appeared at 27 and 35 ppm (ethylene) and 177 ppm (carbonyl)

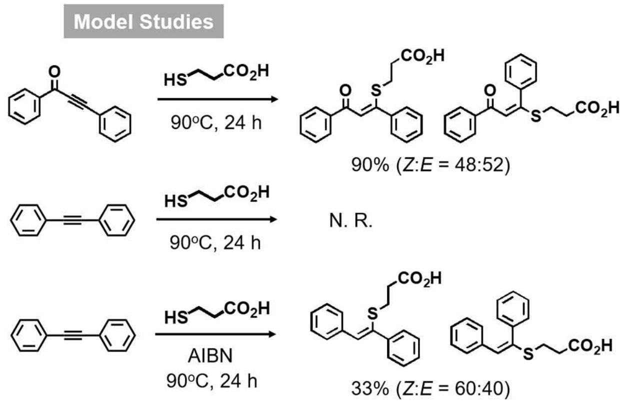

Figure 4. Model studies of 1,3-diphenylpropynone and 1,2-diphenylacetylene toward radical and nonradical thiol-yne reactions with 3-mercaptopropionic acid.

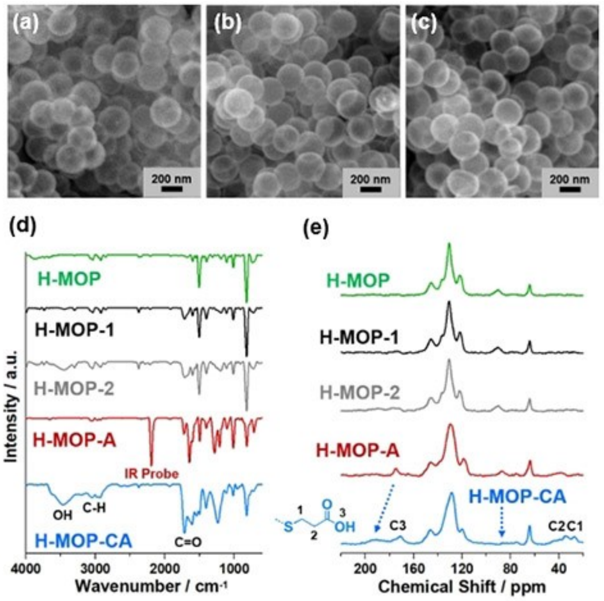

Figure 5. SEM images of (a) H-MOP-CA, (b) H-MOP-1, and (c) H-MOP-2. (d) IR and (e) solid state ^{13}C NMR spectra of H-MOP, H-MOP-1, H-MOP-2, H-MOP-A, and H-MOP-CA. The arrows in the ^{13}C NMR spectrum of H-MOP-CA indicate that the peak of internal alkynes disappeared and that of carbonyl groups shifted to down field through nonradical thiol-yne click-based PSM.

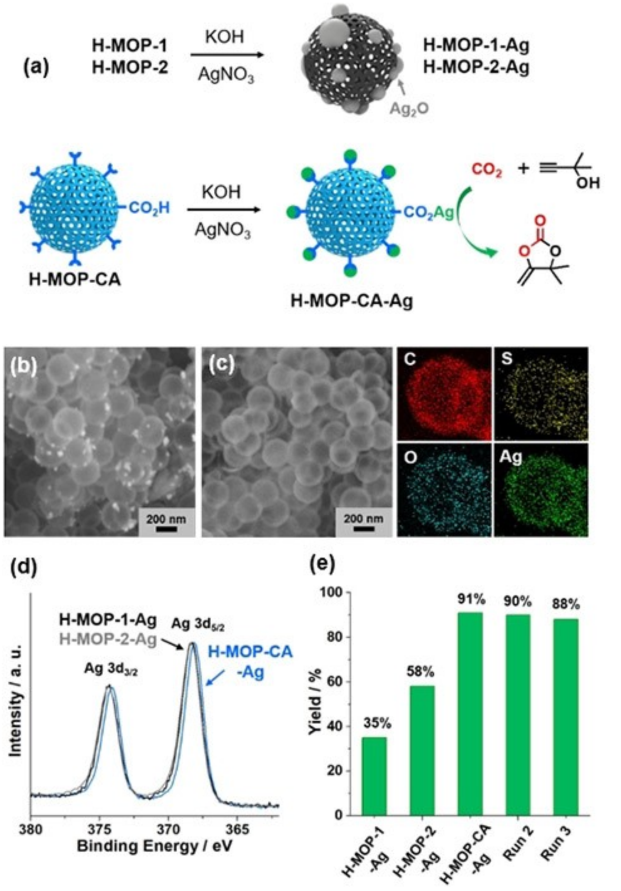

Figure 6. (a) Schemes of Ag incorporation to H-MOP-1, H-MOP-2, and H-MOP-CA. (b) A SEM image of H-MOP-2-Ag (also see Figure S5 in the SI). (c) A SEM image and EDS elemental mapping images of H-MOP-CA-Ag. (d) XPS spectra of Ag 3d orbitals and (e) catalytic performance of H-MOP-1-Ag, H-MOP-2-Ag, and H-MOP-CA-Ag (2 mol% Ag, 1 atm CO_2, 2-methyl-3-butyn-2-ol, toluene, r.t., and 24 h) in the CO_2 fixation to α-alkylidene cyclic carbonates.

(Figure 5e), confirming the successful thiol-yne click-based PSM. While there were no significant changes in the surface areas in the H-MOP-1 (414 m^2/g) and H-MOP-2 (401 m^2/g), compared with that of H-MOP (490 m^2/g), the H-MOP-CA showed a significantly reduced surface area of 45 m^2/g, compared with that of H-MOP-A (346 m^2/g), matching with the observations in the PSM of MOPs in the literature[4] (Figure S2 in the SI). Powder X-ray diffraction (PXRD) studies indicated that all MOPs in this work are amorphous, matching with the conventional properties of MOPs in the literature[1–2] (Figure S4 in the SI).

Next, we studied the applications of H-MOP-CA to develop catalytic systems. Recently, metal-catalyzed CO_2 fixation has attracted great attention from scientists.[16] In 2007, Yamada and coworkers reported that 10 mol% Ag(OAc) can conduct the CO_2 fixation with propargyl alcohols to α-alkylidene cyclic carbonates at room temperature.[17] Since then, the Ag(I)-catalyzed CO_2 fixation has attracted significant attention.[18] Moreover, Ag ions have been grafted onto solid supports such as MOP,[19a–c] carbon, polystyrene, and sulfonated resin.[19–20] To maximize the catalytic activity of Ag(I), its efficient distribution on the supports is critical. It is noteworthy that single-atom and single-site heterogeneous catalysts have attracted great attention of scientists.[21] In this regard, the H-MOP-CA was applied to graft Ag(I) ions, compared with H-MOP-1 and H-MOP-2 (Figure 6a and S5-6 in the SI).

Whilst Ag^+ ions were homogeneously incorporated to H-MOP-CA, irregular Ag_2O particles were loaded on the H-MOP-1 and H-MOP-2 (Figure 6b–c and S5 in the SI). The PXRD patterns of H-MOP-1-Ag and H-MOP-2-Ag showed weak (111) peaks of Ag_2O at $2\theta = 33.2°$ (Figure S6 in the SI). In contrast, H-MOP-CA-Ag was noncrystalline, indicating that Ag^+ ions were homogeneously distributed. ICP analysis indicated that the Ag contents in H-MOP-CA-Ag, H-MOP-1-Ag, and H-MOP-2-Ag were 7.75, 4.77, and 5.99 wt%, respectively. According to XPS studies, while the Ag 3d orbital peaks of H-MOP-1-Ag and H-MOP-2-Ag were observed at 374.4 and 368.3 eV, those of H-MOP-CA-Ag were shifted to 374.1 and 368.1 eV (Figure 6d). In the IR spectrum of H-MOP-CA-Ag, the original carbonyl peak (1717 cm^{-1}) of carboxylic acid was reduced through formation of anionic carboxylate moieties (Figure S7 in the SI). In the solid state ^{13}C NMR spectrum of H-MOP-CA-Ag, a new ^{13}C peak appeared at 171 ppm (Figure S8 in the SI). The XPS, IR, and NMR studies indicate that Ag(I) carboxylate moieties were formed in the H-MOP-CA-Ag.

We tested the catalytic activities of H-MOP-CA-Ag in the Ag-catalyzed CO_2 fixation with propargyl alcohols to cyclic carbonates (Figure 6e). In a control test, the H-MOP-CA showed no reaction in the CO_2 fixation with 2-methyl-3-butyn-2-ol. When we used *2 mol%* Ag of H-MOP-CA-Ag with 2-methyl-3-butyn-2-ol, the reaction showed a 91% yield of α-alkylidene cyclic carbonate under 1 atm CO_2 at room temperature for 24 h.

The catalytic performance of H-MOP-CA-Ag is comparable or superior to the recent Ag-based heterogeneous catalysts.[19c–e,20] For example, under similar reaction conditions (room temperature and 10 h), *10 mol%* Ag-sulfonated resin showed a 91% yield of cyclic carbonate with 1 atm CO_2 and 2-methyl-3-butyn-2-ol.[19e] The excellent catalytic performance of H-MOP-CA-Ag is attributable to its efficient distribution of Ag ions over the hollow MOP support.[11,21] When the same amounts of H-MOP-1-Ag and H-MOP-2-Ag were used under the same reaction conditions, the cyclic carbonates were formed with yields of 35 and 58%, respectively. When 1-ethynyl-cyclohexan-1-ol was used with 2 mol% Ag of H-MOP-CA-Ag, a 74% yield of cyclic carbonate was obtained.

The H-MOP-CA-Ag could be reused in the second and third runs, showing 90 and 88% yields of cyclic carbonates, respectively, 1.6% Ag leaching after third run, and the complete retention of the original morphologies (Figure 6e and S9 in the SI).

In conclusion, this work shows that H-MOP-A can be synthesized through acyl Sonogashira-Hagihara coupling of tetra(4-ethynylphenyl)methane with terephthaloyl chloride at room temperature. The internal alkynes in the H-MOP-A showed enhanced chemical activities and a very sharp IR peak at 2194 cm^{-1}, which could be utilized in the monitoring of its main chain PSM based on nonradical thiol-yne reaction. The resultant H-MOP-CA bearing propionic acid groups could be utilized as a Ag(I) support. The resultant catalytic system showed excellent performance in the CO_2 fixation with propargyl alcohols to α-alkylidene cyclic carbonates. We believe that chemical structures of H-MOP-A can be further diversified through a pre-designed building block approach and tailored PSM.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Microporous organic polymer · Acyl Sonogashira coupling · Post-synthetic modification · Thiol-yne click reaction · Carbon dioxide conversion

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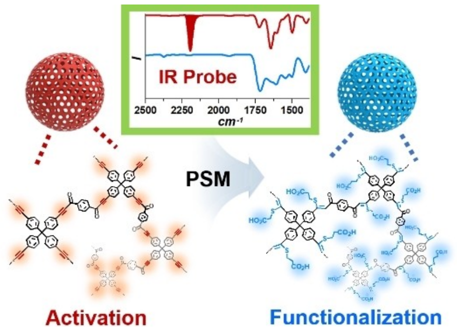
COMMUNICATION



A hollow microporous organic polymer bearing chemically activated alkynes (H-MOP-A) was prepared by an acyl Sonogashira-Hagihara coupling-based template synthesis at room temperature. The H-MOP-A showed IR-monitorable post-synthetic modification based on non-radical thiol-yne click chemistry and applied to Ag(I)-catalyzed CO_2 conversion.

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Room-Temperature Synthesis of a Hollow Microporous Organic Polymer Bearing Activated Alkyne IR Probes for Nonradical Thiol-yne Click-Based Post-Functionalization