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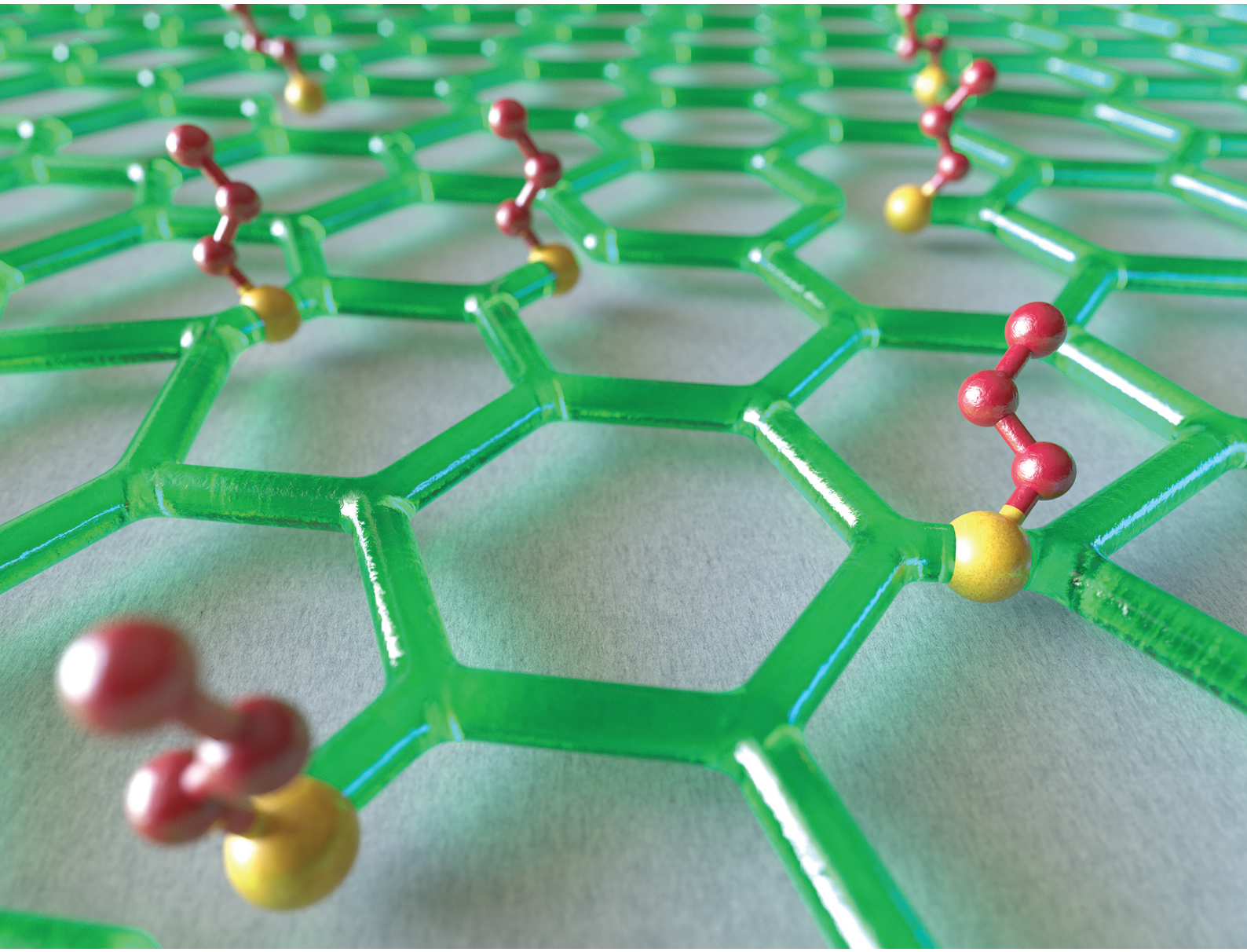

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Kyoung Chul Ko, Seung Uk Son *et al.*

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To which sites were thiols added? Insight into the thiol–yne click-based post-synthetic modification of conjugated microporous polymers†

June Young Jang,[a] Gye Hong Kim,[b] Yoon-Joo Ko,[c] Kyoung Chul Ko *[d] and Seung Uk Son *[a]

A post-synthetic modification (PSM) strategy is useful for the functionalization of conjugated microporous polymers (CMPs). This work shows that the reactivities of chemical moieties in networks are different from those of the isolated molecule state. We suggest that the main chains of CMPs can be chemically inert and the existence of defects is actually critical in the main chain PSM of CMPs. In the thiol–yne click-based main chain PSM of CMPs, thiols were added to defect sites such as 1,3-diynes and dangling alkynes. We suggest that the network-induced resistance for structural strains is the reason for the chemical inertness of the main chains of CMPs. Thus, it can be noted that the unique defective feature of CMPs is beneficial for PSM-based functionalization.

Conjugated microporous polymers (CMPs) are versatile platforms with application in various fields including adsorbents, catalysis, and energy storage.[1] High surface areas and chemical stability have been well recognized as their attractive features.[1] However, the potential benefits of their unique defective features[2] have not attracted much attention from scientists.

The functionality of CMPs can be further diversified by a post-synthetic modification (PSM) strategy.[3] Cohen and other research groups have introduced a PSM strategy in the functionalization of metal–organic frameworks (MOFs).[4] As displayed in Fig. 1, PSM strategies can be divided to two classes, A and B. In class A, building blocks with side functional groups, such as an amino group, are incorporated into porous networks (Fig. 1a).[5–7] Tailored functionalities can be further introduced into the networks through chemical reactions with the side groups. In this case, PSM does not influence the main chain skeleton of the networks.

In class B, CMPs can be functionalized *via* PSM of main chain skeletons.[8–10] For example, thiols have been added to Sonogashira–Hagihara coupling-based CMPs through powerful radical-induced thiol–yne click reactions (Fig. 1b).[11] In class B, while functional groups can be introduced into main chains, the PSM-induced geometrical changes of reaction sites may induce a deviation in the network structure. Thus, it can be speculated that the reactivity of the internal alkynes in the networks of CMPs may be suppressed. Thus, understanding the chemical properties of the main chains of CMPs is necessary for effective functionalization.

In this work, we report the unexpected chemical inertness of main chains of CMPs, the origins of the different chemical reactivities of chemical moieties in molecular and network

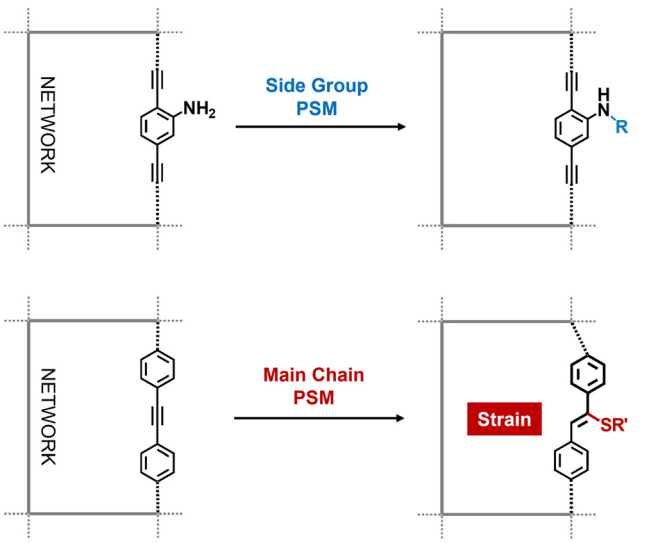

Fig. 1 Post-synthetic modification (PSM) strategies of conjugated microporous polymers (CMPs) *via* the reactions of (a) side groups and (b) main chains of CMPs.

[a]*Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea. E-mail: sson@skku.edu*
[b]*Department of Earth Systems and Environmental Sciences, Chonnam National University, Gwangju 61186, Korea*
[c]*Laboratory of Nuclear Magnetic Resonance, NCIRF, Seoul National University, Seoul 08826, Korea*
[d]*Department of Chemistry Education, Chonnam National University, Gwangju 61186, Korea. E-mail: kcko1982@jnu.ac.kr*

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reactions, and the importance of the defective features of CMPs in PSM-based functionalization.

Recently, scientists including our research group have studied the engineering of functional CMPs based on main chain PSM.[12–17] Generally, CMPs have been prepared by the Sonogashira–Hagihara coupling of multiethynyl arenes and multihalo arenes.[18] Thus, the Sonogashira–Hagihara coupling-based CMPs are rich in alkynes in the main chains. Recently, the thiol–yne click reaction has been utilized for the PSM of CMPs (Fig. 2a).[11–17] However, according to the accumulated solid state ^{13}C nuclear magnetic resonance (NMR) studies, we figured out that after the thiol–yne click-based PSM, most internal alkyne sites of CMPs are actually intact. Thus, we wondered which sites the thiols are actually added to.

As a representative CMP, CMP-1 has been prepared by the Sonogashira–Hagihara coupling of 1,3,5-triethynylbenzene with 1,4-diiodobenzene or 1,4-dibromobenzene in the literature.[18] To induce facile PSM,[19a] we prepared a hollow CMP-1 (H-CMP-1) through the Sonogashira–Hagihara coupling of 1,3,5-triethynylbenzene with 1.5 eq. of 1,4-diiodobenzene in the presence of silica spheres and successive silica etching (Fig. 2b).[19]

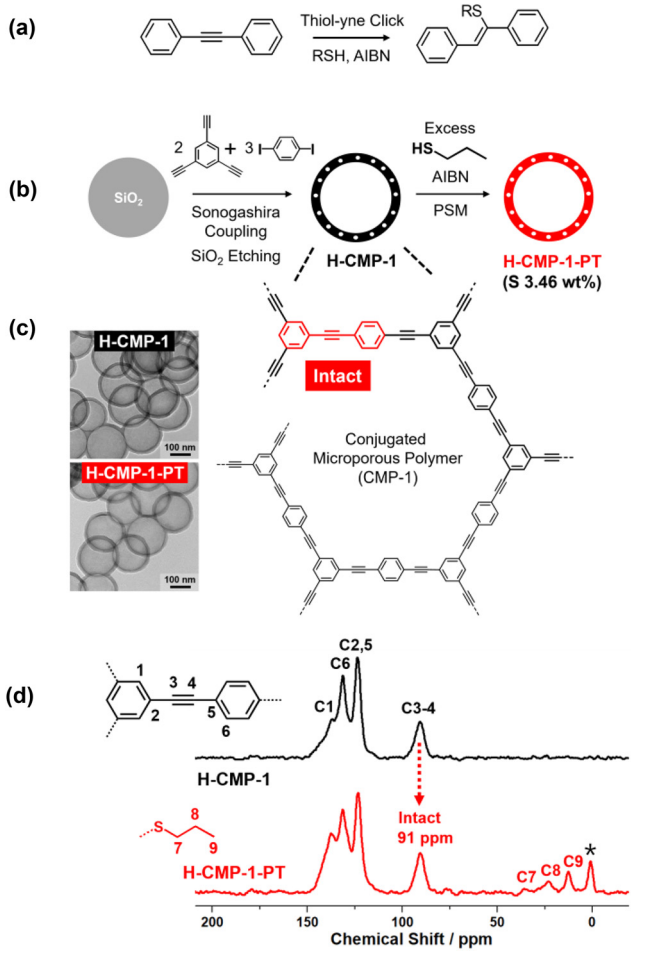

Fig. 2 (a) A model reaction scheme of the thiol–yne click reaction of diphenylacetylene with alkylthiols. (b) A synthetic scheme, (c) TEM images, and (d) solid state ^{13}C NMR CP/TOSS spectra of H-CMP-1 and H-CMP-1-PT. The ^{13}C peak indicated by a black asterisk in (d) corresponds to a silicone grease.

The scanning (SEM) and transmission electron microscopy (TEM) images of H-CMP-1 showed a hollow structure with a diameter and thickness of ~220 and 12–15 nm, respectively (Fig. 2c and S1, 2 in the ESI†). According to the analysis of N_2 sorption isotherm curves based on Brunauer–Emmett–Teller (BET) theory, the surface area of H-CMP-1 was found to be 653 $m^2\ g^{-1}$ (Fig. S3 in the ESI†). The pore size analysis based on the density functional theory (DFT) method revealed the typical microporosity of H-CMP-1 (Fig. S3 in the ESI†).

Following the PSM procedures of the radical-induced thiol–yne reaction in the literature,[11] we reacted H-CMP-1 with excess 1-propanethiol (PT) in the presence of azobis(isobutyronitrile) (AIBN) at 90 °C for 24 h (Fig. 2a and b). We used the small thiol PT to induce efficient PSM, excluding methanethiol and ethanethiol due to their low boiling points. The surface area of the resultant H-CMP-1-PT was reduced to 463 $m^2\ g^{-1}$ with a decrease of micropores (Fig. S3 in the ESI†). The hollow morphology was completely retained in the TEM image of H-CMP-1-PT (Fig. 2c).

The chemical structure of H-CMP-1-PT was analyzed by solid state ^{13}C NMR and infrared (IR) spectroscopy. As shown in Fig. 2d, although we used excess 1-propanethiol, after the PSM, the original ^{13}C peak of internal alkynes at 91 ppm was significantly retained. The ^{13}C peaks at 74–84 ppm of the defective terminal alkynes and 1,3-diynes were not detected in the ^{13}C NMR spectrum of H-CMP-1 (Fig. 2d). The vibration peak at 3290–3300 cm^{-1} of terminal alkynes was infinitesimal (Fig. S4 in the ESI†). The relatively less defective nature of H-CMP-1 is attributable to the 2 : 3 stoichiometric coupling of 1,3,5-triethynyl benzenes with 1,4-diiodobenzenes. The minor ^{13}C peaks of propyl groups appeared at 13, 23, and 35 ppm in the ^{13}C NMR spectrum of H-CMP-1-PT. The IR spectrum of H-CMP-1-PT revealed aliphatic vibration peaks at 2930–2970 cm^{-1} (Fig. S4 in the ESI†). The content of the 1-propylthiolate group was found to be 1.08 mmol g^{-1} by elemental analysis of sulfur (S: 3.46 wt%).

To elucidate the reaction sites of thiol addition, we conducted a model test of iodobenzene with 1-propanethiol under the reaction conditions of the thiol–yne click reaction, showing no conversion (Fig. 3a). This implies that 1-propanethiol was not added to defective aryl iodide sites. We suggest that the chemical inertness of the diphenylacetylene moieties in the main chain of H-CMP-1 might result from the network-induced strain after the 1-propanethiol addition to alkynes in the networks. Thus, we suggest that 1-propanethiol can be added to the defective dangling alkynes in the networks (Fig. 3b).

It is noteworthy that enhanced surface areas of CMPs could be achieved in the literature[18] by the coupling of 1,3,5-triethynylbenzene and 1,4-dibromobenzene at a 1 : 1 ratio. Thus, we prepared another hollow CMP-1 (in this work, we denote as H-CMP-Br for comparison) by the Sonogashira–Hagihara coupling of 1,3,5-triethynylbenzene with 1 eq. of 1,4-dibromoben-

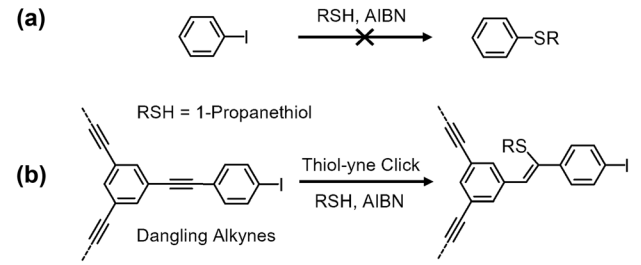

Fig. 3 (a) A model reaction of iodobenzene with 1-propanethiol under the reaction conditions of the thiol–yne click reaction and (b) the suggested PSM process of H-CMP-1 based on the thiol addition to dangling internal alkynes.

zene, followed by the alkyne–alkyne Glaser coupling, to induce the defective feature (Fig. 4a).[2] Through the thiol–yne click-based PSM, we prepared H-CMP-Br-PT. The surface areas decreased from 791 $m^2\ g^{-1}$ to 427 $m^2\ g^{-1}$ with a decrease of micropores due to the PSM of H-CMP-Br to H-CMP-Br-PT (Fig. S3 in the ESI†). The hollow morphologies of H-CMP-Br with a diameter and thickness of ~220 and 12–15 nm, respectively, were completely retained in H-CMP-Br-PT (Fig. 4b and S1, 2 in the ESI†).

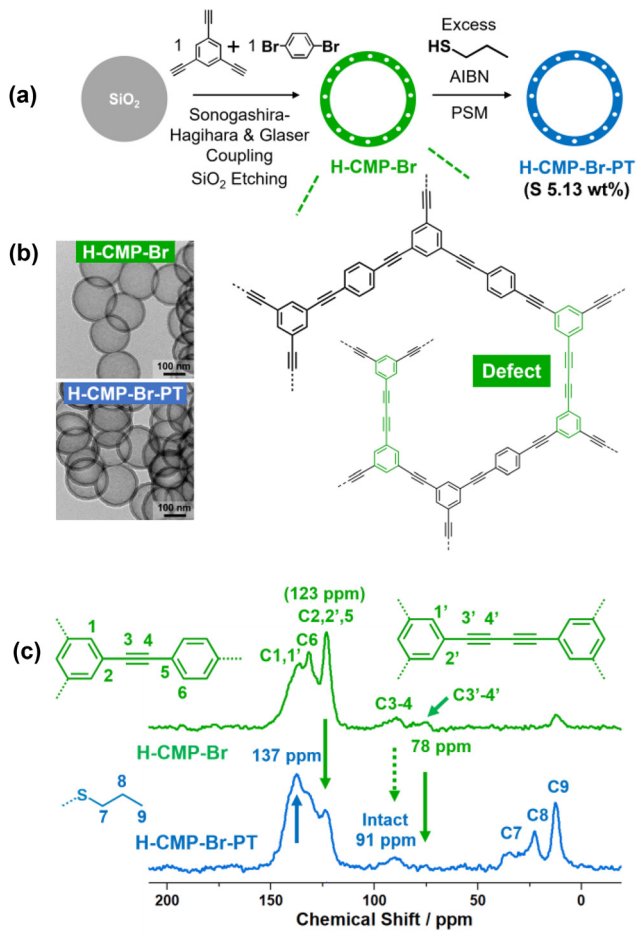

Fig. 4 (a) A synthetic scheme, (b) TEM images, and (c) solid state ^{13}C NMR CP/TOSS spectra of H-CMP-Br and H-CMP-Br-PT.

The ^{13}C peaks of alkynes in the solid state ^{13}C NMR spectrum of H-CMP-Br were significantly different from those of H-CMP-1. The intensity of the internal alkyne ^{13}C peak at 91 ppm was significantly reduced (Fig. 4c). Instead, other ^{13}C peaks appeared at 74–85 ppm, corresponding to the defective terminal alkynes or 1,3-diynes.[20] In the IR spectrum of H-CMP-Br, the terminal alkyne peak at 2950–3300 cm^{-1} was infinitesimal (Fig. S4 in the ESI†), indicating that the ^{13}C peaks of 74–85 ppm of H-CMP-Br are mainly attributable to 1,3-diynes.[20] Interestingly, while the internal alkyne ^{13}C peak at 91 ppm was retained after the PSM, those of 1,3-diynes disappeared in the ^{13}C NMR spectrum of H-CMP-Br-PT, indicating that the PSM occurred at 1,3-diyne sites (Fig. 4c). The intensities of ^{13}C peaks at 123 ppm significantly decreased with an increase of the intensities of ^{13}C peaks at 137 ppm due to the PSM of H-CMP-Br to H-CMP-Br-PT (Fig. 4c). The intensities of propyl ^{13}C peaks at 13, 23, and 35 ppm of H-CMP-Br-PT significantly increased, compared with those of H-CMP-1-PT (Fig. 2d and 4c). In addition, the aliphatic vibration peaks at 2930–2970 cm^{-1} were enhanced in the IR spectrum of H-CMP-Br-PT (Fig. S4 in the ESI†). Elemental analysis revealed that the amount of the incorporated propylthiolate groups is 1.60 mmol g^{-1} (S: 5.13 wt%). These observations indicate that PSM was enhanced with the defective 1,3-diynes of H-CMP-Br, compared with that of H-CMP-1, in addition to the PSM of the dangling internal alkynes of connection defects.

A candidate conversion in the PSM of H-CMP-Br can be the thiolate substitution of defective aryl bromide, which is expected to show the same change of the ^{13}C peak from 123 ppm to 137 ppm. However, in the presence or absence of Pd and Cu catalysts, bromobenzene showed no reactions whatsoever (Fig. 5a). Thus, the possible addition of propylthiolates to defective aryl bromides in H-CMP-Br can be excluded. In comparison, alkyl thiols were added to the 1 and 4 positions of 1,4-diphenyl-1,3-diyne in the model thiol–yne click reaction[21,22] (Fig. 5b and S5, 6 in the ESI†). The ^{13}C peak at

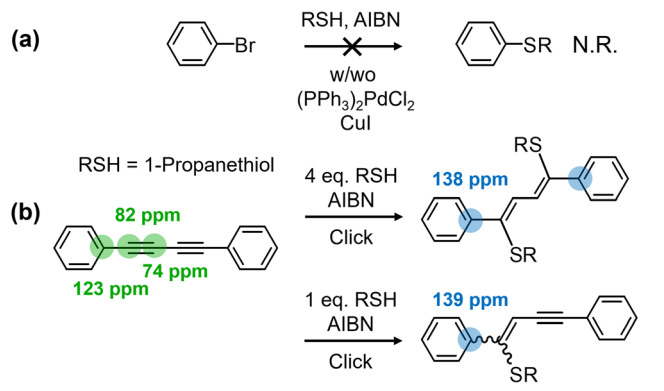

Fig. 5 (a and b) Model reactions for the possible PSM processes of H-CMP-Br based on the thiol–yne click reaction of 1-propanethiol (refer to Fig. S5, 6 in the ESI†).

123 ppm shifted to 138–139 ppm after the thiol addition, matching well with the observation in the PSM of H-CMP-Br.

Next, to study the PSM of a 1,3-diyne-rich CMP, we prepared H-CMP-G by the Glaser self-coupling of 1,3,5-triethynylbenzene[23] (Fig. 6a). After the PSM of H-CMP-G by the thiol–yne click reaction, we obtained H-CMP-G-PT. The hollow morphologies of H-CMP-G with a diameter and thickness of ~220 and 12–15 nm, respectively, were completely retained in H-CMP-G-PT (Fig. 6b and S1, 2 in the ESI†).

In the IR spectrum of H-CMP-G, the vibration peak of terminal alkynes at 3301 cm^{-1} was not detected (Fig. S4 in the ESI†). In the ^{13}C NMR spectra, the ^{13}C peaks of the 1,3-diynes at 74–82 ppm disappeared due to the PSM, indicating that thiols were mostly added to the 1,3-diynes (Fig. 6c). The surface area decreased from 670 $m^2\ g^{-1}$ to 208 $m^2\ g^{-1}$ with a decrease of micropores due to the PSM of H-CMP-G to H-CMP-G-PT (Fig. S3 in the ESI†). In the IR spectrum of H-CMP-G-PT, the aliphatic vibration peaks at 2930–2970 cm^{-1} were significantly enhanced (Fig. S4 in the ESI†). In addition, the intensities of the ^{13}C peaks at 13, 23, and 35 ppm were enhanced (Fig. 6c). As expected, the ^{13}C peak at 123 ppm decreased with an increase of the ^{13}C peak at 138 ppm, matching well with the model studies in Fig. 5b and S5, 6 in the ESI.† The content of the incorporated propylthiolate was found to be 1.77 mmol g^{-1} (S: 5.67 wt%). These observations indicate that 1,3-diynes are good reaction sites for thiol–yne click-based PSM.

To rationalize the different reactivities of H-CMP-1 from H-CMP-G towards thiol addition to alkynes, we conducted density functional theory (DFT)-based computational calculations within periodic boundary conditions (Fig. 7 and S7–9 in the ESI†). The suppressed reactivity of internal alkynes toward thiols can be interpreted using the network effect. We calculated the possible structural strains that can occur due to the thiol addition to the ideal network structures of H-CMP-1 and H-CMP-G.

As shown in Fig. 7a and b, the ideal structures of H-CMP-1 and H-CMP-G were simulated as hexagonal networks. For each case, the thiols can be added to two carbon sites of alkynes. The strain energy of networks for the thiol-addition to alkynes was defined as $\Delta E_{strain} = E_{fix} - E_{full}$, where E_{fix} and E_{full} are the self-consistent field (SCF) energy for the optimized thiol-added

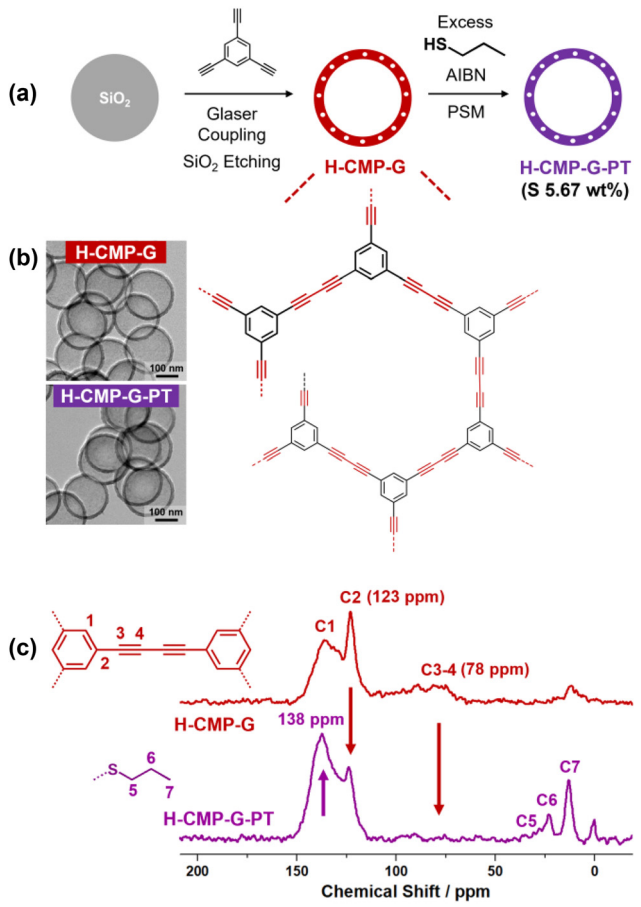

Fig. 6 (a) A synthetic scheme, (b) TEM images, and (c) solid state ^{13}C NMR CP/TOSS spectra of H-CMP-G and H-CMP-G-PT.

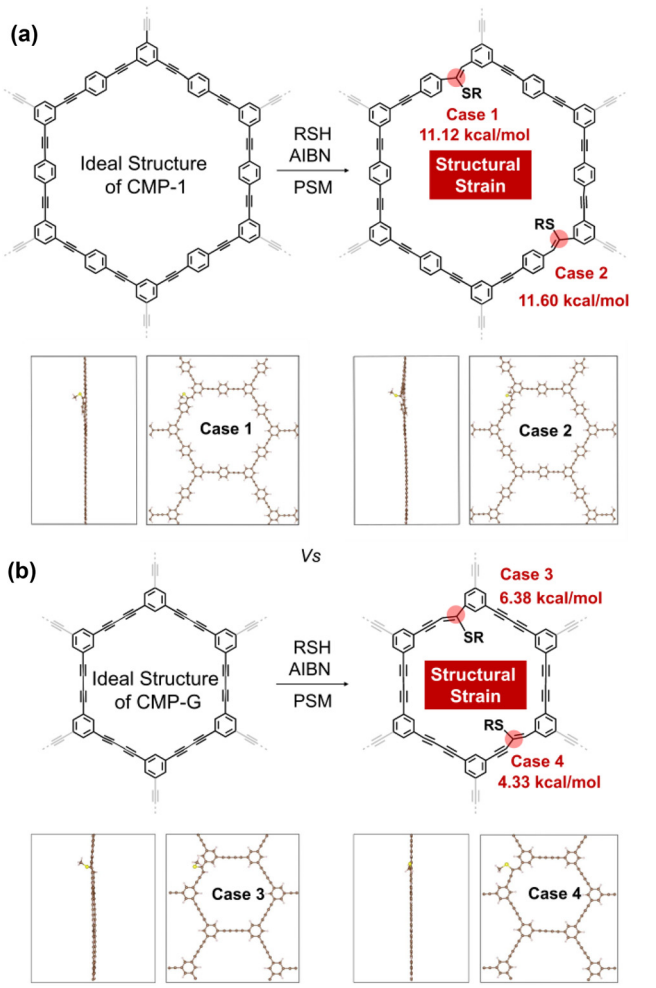

Fig. 7 Calculated strain energies of the ideal network structures of (a) H-CMP-1 and (b) H-CMP-G networks towards the thiol addition to diaryl alkynes and diaryl 1,3-alkynes and the simulated thiol-added network structures.

network structures with fixed benzene ring positions and the SCF energy for fully optimized thiol-added network structures, respectively (refer to the Experimental section in the ESI† for details). For the ideal structure of H-CMP-1, the strain energies for thiol addition to alkynes (indicated as Case 1 and 2 in Fig. 7a) were calculated to be 11.12 and 11.60 kcal mol^{-1}, respectively. In comparison, for the ideal structure of H-CMP-G, the strain energies for thiol addition to alkynes (indicated as Case 3 and 4 in Fig. 7b) were calculated to be 6.38 and 4.33 kcal mol^{-1}, respectively. The differences of structural strains in the ideal network structures of H-CMP-1 and H-CMP-G are attributable to the different structural deviations of networks due to the thiol addition to the diaryl alkyne and diaryl 1,3-diyne moieties. From this information, although H-CMP-1 and H-CMP-G have nonideal networks, the enhanced reactivity of H-CMP-G can be rationalized, compared with that of H-CMP-1.

Based on the experimental and theoretical results, we suggest a thiol–yne click-based PSM process of the CMP materials as displayed in Fig. 8. First, the CMP materials are amorphous and defective (Fig. S10 in the ESI†). Thus, they contain defective dangling internal alkynes, aryl halides, and 1,3-diynes. Among these defects, the aryl halides were inert in the thiol–yne click-based PSM. The relative amount of the dangling internal alkynes may be minor. The 1,3-diyne moieties in the CMP materials can be efficient PSM sites in the main chain functionalization based on the thiol–yne click reaction.

Considering the structural strains and defects, the incorporation of propylthiolate into CMPs is expected to be dependent on reaction temperature. Thus, we investigated PSM contents depending on reaction temperature. As reaction temperature increased from 90 °C to 140 °C (*o*-xylene as solvent), the contents of the incorporated propylthiolate in H-CMP-1-PT increased from 1.08 mmol g^{-1} (S: 3.46 wt%) to 1.34 mmol g^{-1} (S: 4.31 wt%), respectively. Under the same conditions, the contents of the incorporated propylthiolate in H-CMP-Br-PT increased from 1.60 mmol g^{-1} (S: 5.13 wt%) to 1.95 mmol g^{-1} (S: 6.29 wt%), respectively. In the case of H-CMP-G-PT, the contents of the incorporated propylthiolate increased from 1.77 mmol g^{-1} (S: 5.67 wt%) to 2.13 mmol g^{-1} (S: 6.83 wt%), respectively.

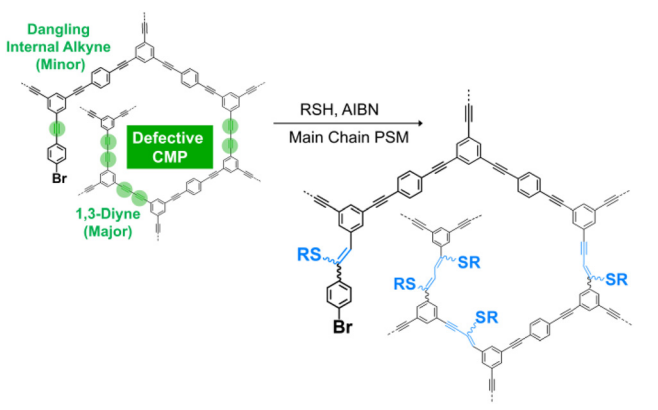

Fig. 8 A suggested main chain PSM process of a defective CMP by thiol–yne click reactions.

In conclusion, this work suggests that most internal alkyne sites in the main chain of CMPs are inert toward the thiol–yne click-based PSM because the inevitable geometric changes of network structures can suppress the reactivity of internal diaryl alkynes. Instead, the connection defects of CMPs can be reaction sites for main chain PSM. Particularly, we suggest that diaryl 1,3-diynes are major reaction sites of thiol–yne click-based PSM, in addition to defective dangling internal alkynes. We believe that this suggestion can be helpful information in the PSM of CMP materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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