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Morphology engineering of a Suzuki coupling-based microporous organic polymer (MOP) using a Sonogashira coupling-based MOP for enhanced nitrophenol sensing in water†

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The morphology of a Suzuki coupling-based microporous organic polymer (SUM) was controlled by the use of a Sonogashira coupling-based microporous organic polymer (SOM). The template synthesis resulted in water compatible and hollow SOM@SUM materials bearing tetraphenylethylene moieties (H-SOM@SUM-T), which showed aggregation-induced emission and promising sensing performance towards nitrophenols in water.

Recently, various Suzuki coupling-based microporous organic polymers (for simplicity, we term these materials SUMs in this work) have been reported.¹ The SUMs have been applied for various purposes, including photocatalysis for H₂ production^{1c} and the emission-based sensing of harmful compounds.^{1d,e} The functional performance of a microporous organic polymer (MOP) is dependent on its morphological structure.² For example, hollow MOPs have shown enhanced catalytic activities due to the reduced diffusion pathways of substrates in the materials.³

During the last decade, our research group⁴ has reported engineering of various morphologies of Sonogashira coupling based-MOPs⁵ (for simplicity, we call these materials SOMs in this work). In comparison, it is surprising that as far as we are aware, the hard template synthesis of SUMs has not been reported.¹ Thus, we have tried to extend the template synthesis to SUM (Fig. 1a–c). However, the results were not successful. We figured out that the reactivity of bases towards silica templates is critical in the successful morphological engineering of MOPs. In the case of Sonogashira coupling, the relatively weak amines have been used as bases to help in the abstraction of protons

from acidic terminal alkynes. In comparison, in the Suzuki coupling, relatively stronger bases, such as K₂CO₃, have frequently been used. It was suggested that these bases help not only in the transmetalation of aryl groups in aryl boronic acids through the formation of anionic borate species but also in the replacement of halide in Pd-halide species with aryl ligands.⁶ When we used the silica spheres as templates in the morphological engineering of SUM, new solid materials formed exclusively. Our powder X-ray diffraction (PXRD) analysis confirmed that the solids are KHSi₂O₅, which are formed by the reaction of silica with K₂CO₃ (Fig. 1b and Fig. S1 in the ESI†). Eventually, the consumption of original bases and silica templates resulted in failure in the morphological engineering of SUM.

We devised the use of hollow SOM as a template for the engineering of hollow SUM. It is noteworthy that the SOM prepared

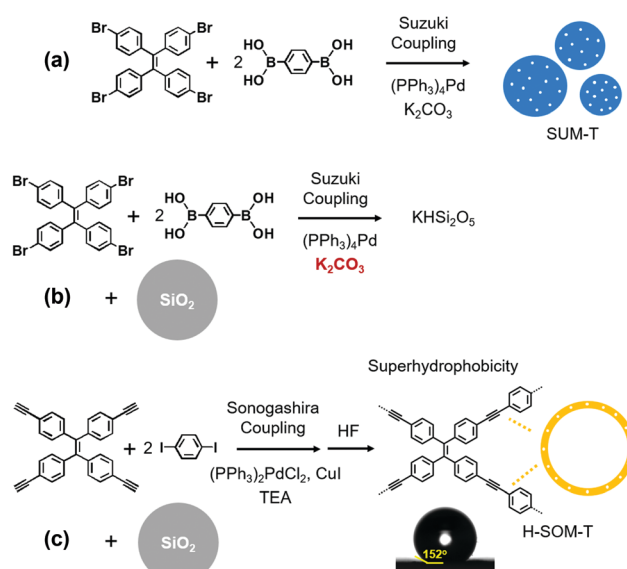


Fig. 1 (a) A synthetic scheme for SUM-T. (b) A trial for the template synthesis of SUM-T using silica spheres. (c) Synthesis of H-SOM-T and its water contact angle showing superhydrophobicity.

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using by the Sonogashira coupling of tetra(4-ethynylphenyl)-ethylene with 1,4-diiodobenzene is superhydrophobic with a water contact angle of 152° and not dispersible in water (Fig. 1c). In comparison, the SUM prepared by the Suzuki coupling of tetra(4-bromophenyl)ethylene with benzene-1,4-diboronic acid is hydrophilic and water-dispersible (Fig. S2 in the ESI†). Actually, the SOMs and SUMs are rich in defects. While the SOMs are rich in aryl halides, the SUMs are rich in aryl boronic acids (Fig. 2). The boronic acid defects in the SUMs resulted in their water-dispersibility.

The emissive MOPs, including those based on the aggregation-induced emission (AIE), have been applied for the detection of harmful compounds.^{1d,e,7–9} However, the use of water only as a sensing medium has been less explored⁸ and additional organic solvents were required^{1d,e,7,9} (Table S1 in the ESI†). In this work, we report the engineering of hollow SOM@SUM bearing tetraphenylethylene moieties (H-SOM@SUM-T) and their application for the sensing of nitrophenols in water.

Fig. 2 shows a synthetic strategy of H-SOM@SUM-Ts using H-SOM as a template. First, by the Sonogashira coupling of

tetra(4-ethynylphenyl)methane with 1,4-diiodobenzene in the presence of silica spheres and the successive etching of templates, we prepared H-SOM. Using the H-SOM as a template, we conducted the Suzuki coupling of tetra(4-bromophenyl)-ethylene with benzene-1,4-diboronic acid to form H-SOM@SUM-T. By increasing the amount of building blocks, we prepared three kinds of H-SOM@SUM-T with relatively thinnest, thinner, and thickest shells, which are denoted in this work as H-SOM@SUM-T1, H-SOM@SUM-T2, and H-SOM@SUM-T3, respectively. The H-SOM and H-SOM@SUM-Ts were investigated by scanning (SEM) and transmission electron microscopy (TEM) (Fig. 3a–d).

The SEM images of H-SOM and H-SOM@SUM-Ts showed the overall hollow morphologies of materials (Fig. 3a–d). According to TEM analysis, the shell thicknesses gradually increased from 13 nm (H-SOM) to 16 nm (H-SOM@SUM-T1), 20 nm (H-SOM@SUM-T2), and 27 nm (H-SOM@SUM-T3) through the incorporation of SUM-T materials on the H-SOM platform (Fig. 3a–d). As the thickness of SUM-T in H-SOM@SUM-T increased, water contact angles gradually decreased from 152° (superhydrophobicity, H-SOM) to 75° (H-SOM@SUM-T1), 48° (H-SOM@SUM-T2), and 31° (H-SOM@SUM-T3) with an increase of hydrophilicity, due to the hydrophilic boronic acid groups (refer to B and O mapping images in Fig. 3c).

While the surface areas of H-SOM and SUM-T were measured to be 682 and $476 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. 4a), those of H-SOM@SUM-T1, H-SOM@SUM-T2, and H-SOM@SUM-T3

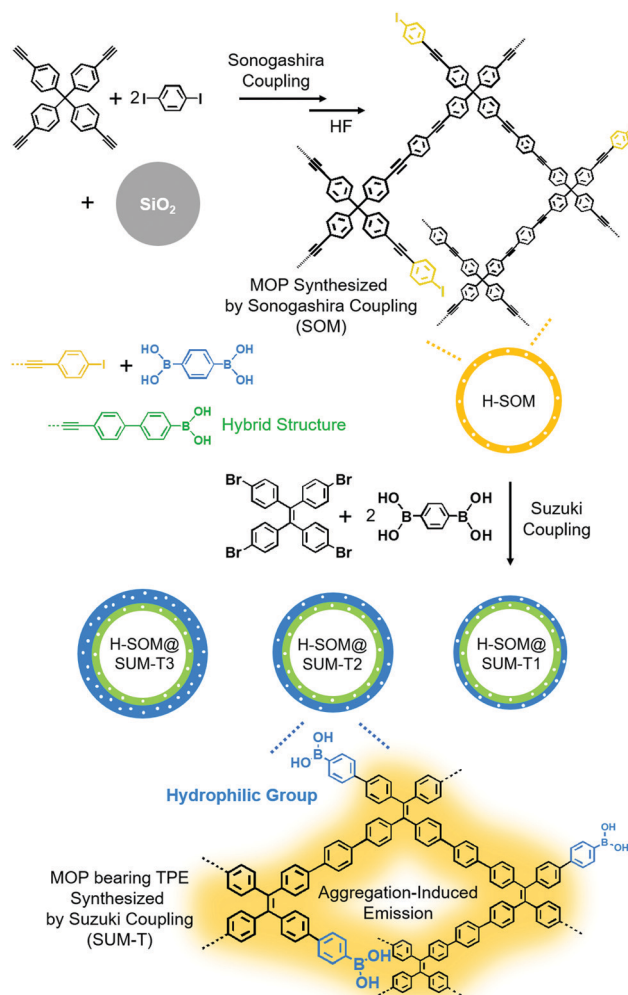


Fig. 2 Template synthesis of H-SOM@SUM-T using H-SOM.

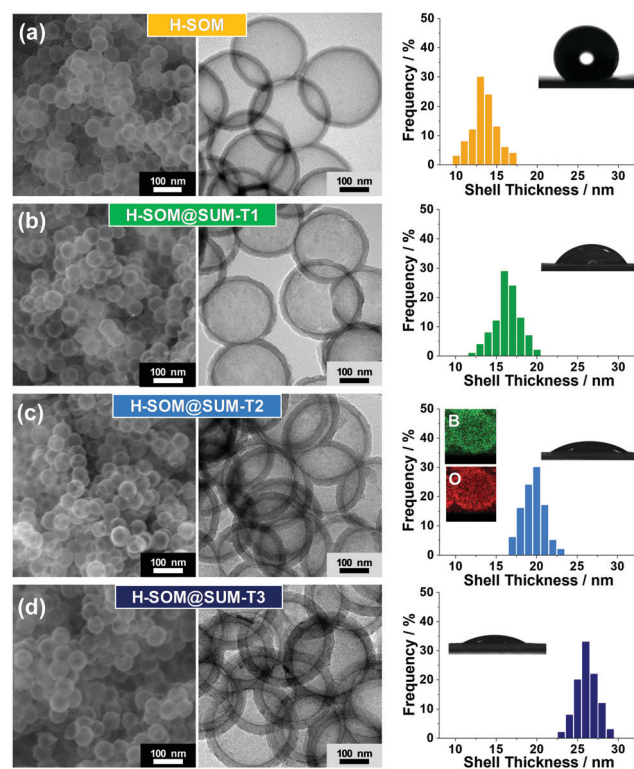


Fig. 3 SEM and TEM images, shell thickness distribution diagrams, and water contact angles of (a) H-SOM, (b) H-SOM@SUM-T1, (c) H-SOM@SUM-T2, and (d) H-SOM@SUM-T3. (c) EELS elemental mapping images of B and O in H-SOM@SUM-T2.

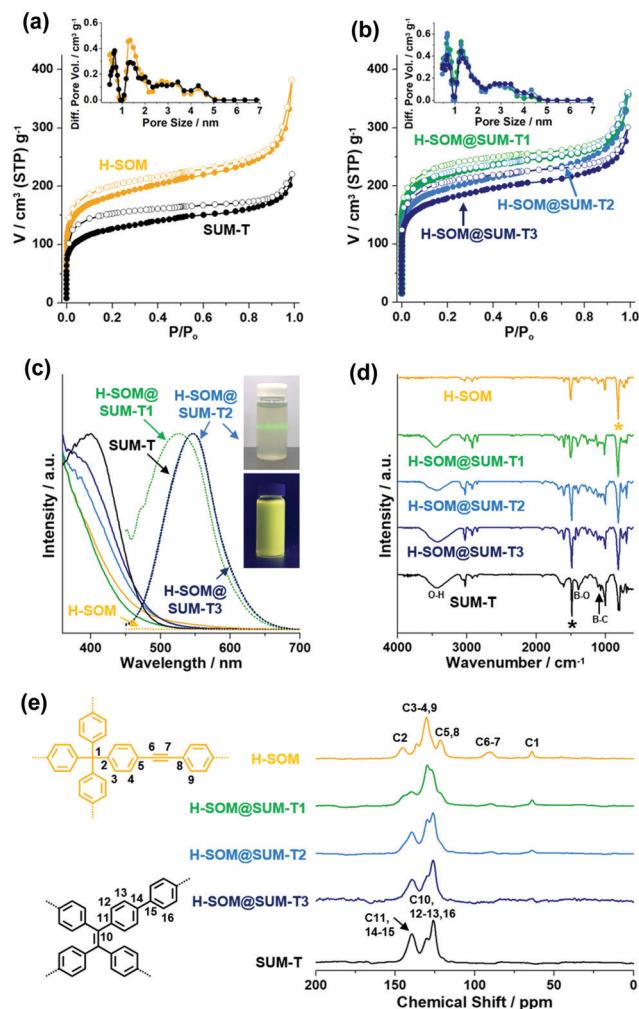


Fig. 4 (a and b) N_2 sorption isotherm curves obtained at 77 K and pore size distribution diagrams (the DFT method), (c) UV/vis absorption and emission spectra (inset: the photographs of H-SOM@SUM-T2 in water, $\lambda_{\text{ex}} = 410$ nm), (d) IR absorption spectra, and (e) solid state ^{13}C NMR spectra of H-SOM, SUM-T, and H-SOM@SUM-Ts.

were measured to be 817, 724, and $666 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. 4b). All of the MOP materials showed microporosity (pore sizes < 2 nm) and amorphous features (Fig. 4a, b and Fig. S3 in the ESI[†]). As the amount of SUM-T in H-SOM@SUM-T increased, the UV/visible absorption peaks were gradually red-shifted due to the elongated conjugation lengths of the materials (Fig. 4c). As shown in photographs in Fig. 4c, H-SOM@SUM-T2 was highly dispersible and emissive in water with an emission quantum yield of 0.78. While H-SOM@SUM-T1 in water showed emission at 517 nm, possibly due to the hybrid structure formed between the aryl iodide defects of H-SOM and benzene-1,4-diboronic acid, H-SOM@SUM-T2–T3 and SUM-T showed aggregation-induced emission at 547 nm in water (Fig. 2 and 4c).

The infrared (IR) spectroscopy spectrum of H-SOM showed the major C=C and C–H vibrations of aromatic groups at 1503 and 820 cm^{-1} , respectively (Fig. 4d). As the amount of SUM-T increased in H-SOM@SUM-T, the peak intensities at 1490 cm^{-1} of SUM-T increased. The solid state ^{13}C nuclear magnetic resonance

(NMR) spectrum of H-SOM showed the ^{13}C peaks of benzyl carbon, alkynes, and aromatic groups at 64, 87–95, and 121–146 ppm, respectively. As the amount of SUM-T increased in H-SOM@SUM-T, the ^{13}C peaks of SUM-T at 126 and 139 ppm relatively increased.

Nitrophenols are known to be intermediates that are generated in the industrial synthesis of drugs, dyes, and pesticides and their detection is an important environmental issue.¹⁰ Considering the water-compatibility and emissive feature of H-SOM@SUM-Ts, we studied their emission quenching-based sensing performance towards nitrophenols in water. Fig. 5 and Fig. S4, Table S1 in the ESI[†] summarize the results.

The order of sensing efficiency for 2,4,6-trinitrophenol (TNP) in water was H-SOM@SUM-T2 $>$ H-SOM@SUM-T3 $>$ H-SOM@SUM-T1 $>$ SUM-T (Fig. 5a–d). Due to their superhydrophobicity, H-SOM-T and H-SOM could not be applied to the sensing of nitrophenols in water. Through the Stern–Volmer plots, the K_{SV} values of H-SOM@SUM-T2, H-SOM@SUM-T3, H-SOM@SUM-T1, and SUM-T towards TNP were measured to be 7.3×10^4 , 4.9×10^4 ,

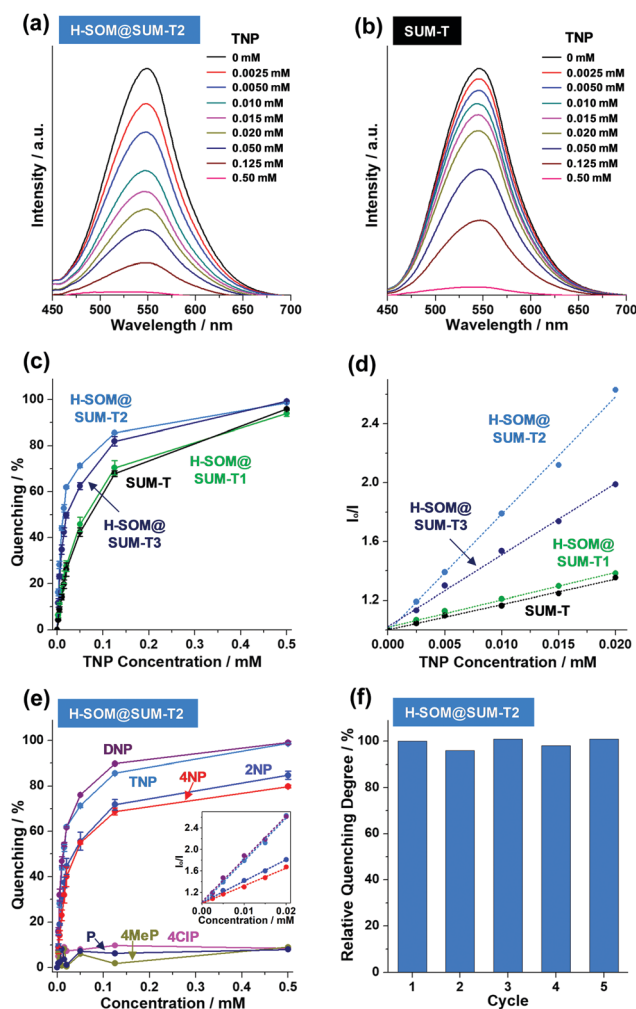


Fig. 5 Emission spectra of H-SOM@SUM-T2 (a) and SUM-T (b) in the presence of TNP. (c) Emission quenching and (d) the corresponding Stern–Volmer plots of H-SOM@SUM-T materials and SUM-T in the presence of TNP. (e) Substrate dependent emission quenching and (f) recyclability (0.5 mM TNP) of H-SOM@SUM-T2.

1.9×10^4 , and $1.7 \times 10^4 \text{ M}^{-1}$, respectively (Fig. 5d). The limits of detection (LOD) of H-SOM@SUM-T2, H-SOM@SUM-T3, H-SOM@SUM-T1, and SUM-T towards TNP were measured to be 0.15, 0.30, 0.52, and 0.56 ppm, respectively. In the AIE quenching-based sensing,⁷ the thickness of materials is a critical factor because the shorter diffusion pathways of sensing targets can result in more facile interaction of substrates with AIE moieties in the materials. Thus, as the thickness of SUM-T in H-SOM@SUM-Ts decreases, the sensing efficiency increases. However, as the thickness of SUM-T in H-SOM@SUM-T decreases, the water compatibility of the materials decreases due to the superhydrophobic H-SOM. By the optimization of these opposite factors, H-SOM@SUM-T2 might show the best performance.

Among the nitrophenols, the order of sensing efficiency was TNP $\sim$ 2,4-dinitrophenol (DNP) $>$ 2-nitrophenol (2NP) $>$ 4-nitrophenol (4NP) (Fig. 5e). The emission of H-SOM@SUM-T2 was not quenched by phenol (P), 4-chlorophenol (4ClP), or 4-methylphenol (4MeP) (Fig. 5e). The LUMO and HOMO energy levels of H-SOM@SUM-T were simulated at -2.32 and -5.41 eV, respectively (Fig. S5–S7 in the ESI†). The LUMO energy levels of TNP, DNP, 4NP, 2NP, phenol, 4-chlorophenol, and 4-methylphenol were simulated at -4.38 , -3.28 , -3.23 , -2.77 , -0.52 , -0.92 , and -0.47 eV, respectively. The observed sensing ability of H-SOM@SUM-T is attributable to the degrees of facile electron transfer from the excited state of H-SOM@SUM-T to the LUMOs of phenol derivatives and the size effect of substrates (Fig. S8 in the ESI†). Thermogravimetric analysis showed that H-SOM@SUM-T2 was stable up to 365°C (Fig. S9 in the ESI†). Considering the stability, we tested the recyclability of H-SOM@SUM-T2. As shown in Fig. 5f, H-SOM@SUM-T2 maintained the original sensing performance in the five successive sensing tests. The SEM and IR absorption studies of H-SOM@SUM-T2 recovered after five sensing tests showed complete retention of the original hollow structure and chemical structure (Fig. S10 in the ESI†). In the literature,^{1d,7b,c,9} the most sensing studies of emissive MOPs towards nitrophenols required additional organic media due to the hydrophobic nature of MOPs and showed K_{sv} values in the range of 2.08×10^3 – $6.4 \times 10^4 \text{ M}^{-1}$ (Table S1 in the ESI†). The corresponding studies in water for the sensing of nitrophenols are quite rare and showed K_{sv} values up to $3.37 \times 10^4 \text{ M}^{-1}$ with LODs up to 0.23 ppm.⁸ The sensing performance (K_{sv} ; $7.3 \times 10^4 \text{ M}^{-1}$, LOD; 0.15 ppm for TNP) of H-SOM@SUM-T2 in water is superior to those of the recent emissive MOPs in the literature, due to the thin thickness, porosity, and hydrophilicity of SUM^{1d,7b,c,8,9} (Table S1 in the ESI†).

In conclusion, this work shows that the hollow SOM can be utilized for the morphological engineering of the SUM. The synthesized H-SOM@SUM-T showed promising sensing performance towards nitrophenols in water, due to the hollow morphology and the water-compatibility. We believe that the shape-engineered SOM materials can be further utilized

for the engineering of other MOPs based on various coupling reactions.

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Conflicts of interest

There are no conflicts to declare.

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