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Hollow Microporous Organic Networks Bearing Triphenylamines and Anthraquinones: Diffusion Pathway Effect in Visible Light-Driven Oxidative Coupling of Benzylamines

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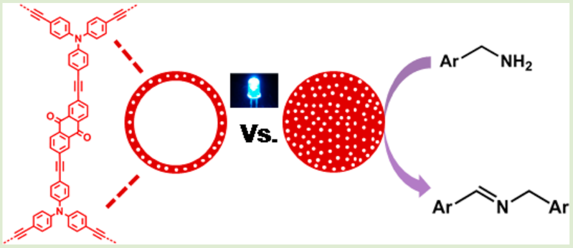
Supporting Information

ABSTRACT: Hollow microporous organic networks were prepared by using silica spheres as the template and tris(4-ethynylphenyl)amine and 2,6-diiodo-9,10-anthraquinone as the building blocks for the Sonogashira coupling. The resultant materials bearing triphenylamine and anthraquinone moieties showed efficient visible light absorption and catalytic activities in the photochemical oxidative coupling of benzylamines. Through the comparison studies of hollow and nonhollow catalytic materials, the diffusion pathway effect of the substrates was clearly observed in the photochemical conversion of benzylamines.



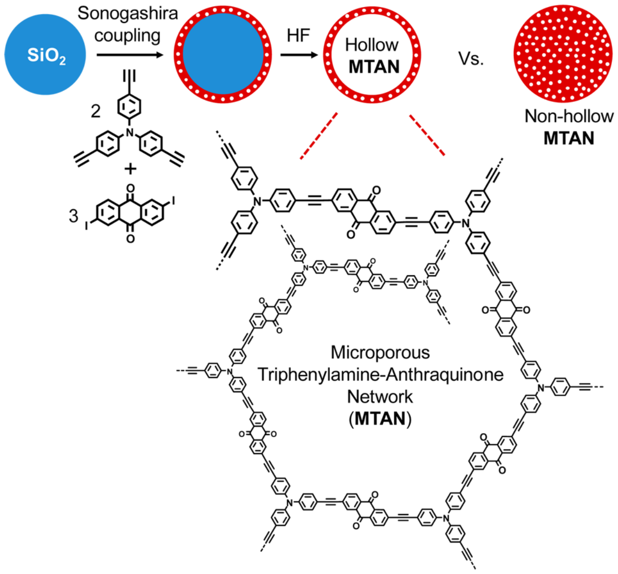
In recent years, microporous organic networks (MONs) have attracted great attention as versatile functional materials.[1] For example, the Cooper group has shown the synthesis of MONs via the Sonogashira coupling of alkynes and arylhalides.[2] Using the tailored building blocks, the target functions could be incorporated into MONs.[3] Among various functions of MONs, the optical properties have attracted significant attention.[4] The light absorption and emission properties of the conjugated MONs have been studied.[4] For the visible light harvesting, the visible light absorbing moieties such as $[Ru(bpy)_3]^{2+}$ or $[Ir(PPy)_2(bpy)]^+$ were incorporated to MONs.[4a] Moreover, the conjugated extension of building blocks resulted in the red-shift of the absorption to the visible light region.[4g] These MONs could promote photochemical reactions under visible light irradiation.[4a,g]

Usually, MONs show high surface area and microporosity (pore size < 2 nm).[1] Based on these properties, the inner moieties of MONs can be utilized in chemical transformations. In another aspect, the structural shape of MONs can be related to the diffusion pathway of substrates for the chemical transformation. The diffusion pathway can be a critical factor in the chemical conversion by porous systems.[5] However, as far as we are aware, there were no reports on the structural shape-related diffusion pathway effect of MONs. Our group has studied the functional MONs[6] and recently reported the structural shape engineering of MONs.[7] In addition, we reported that the introduction of electron deficient groups to arylamine derivatives resulted in visible light absorbing molecules.[8] In this study, we report the synthesis of visible light harvesting hollow MONs and the diffusion pathway effect in visible light-driven oxidative coupling of benzylamines.

Scheme 1 shows the synthetic method for the hollow MONs bearing triphenylamine and anthraquinones.

Tris(4-ethynylphenyl)amine and 2,6-diiodo-9,10-anthraquinone were prepared as the building blocks by the literature

Scheme 1. Synthesis of Hollow and Nonhollow Microporous Triphenylamine-Anthraquinone Networks (MTANs)



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methods.[9] Using silica spheres, MONs were formed on the surface of the silica templates. After etching the silica via the HF treatment, the hollow microporous triphenylamine-anthraquinone networks (hollow **MTAN**s) were prepared. As the control materials, nonhollow **MTAN**s were prepared without using silica spheres. The transmission electron microscopy (TEM) images in Figure 1a,b show the hollow **MTAN** spheres with a diameter and shell thickness of 100 and 20 nm, respectively. The TEM image in Figure 1c shows the polydispersed nonhollow **MTAN**s. The N_2 isotherm analysis showed 574 and 568 m^2/g surface areas for hollow and nonhollow **MTAN**s, respectively. (Figure 1d) The pore size distribution analysis by the density functional theory (DFT method) showed the microporosity of the **MTAN**s (inset in Figure 1d). According to the powder X-ray diffraction studies, the **MTAN** materials have amorphous characteristic, as commonly observed in MONs[1,2] (Figure S1 in the SI).

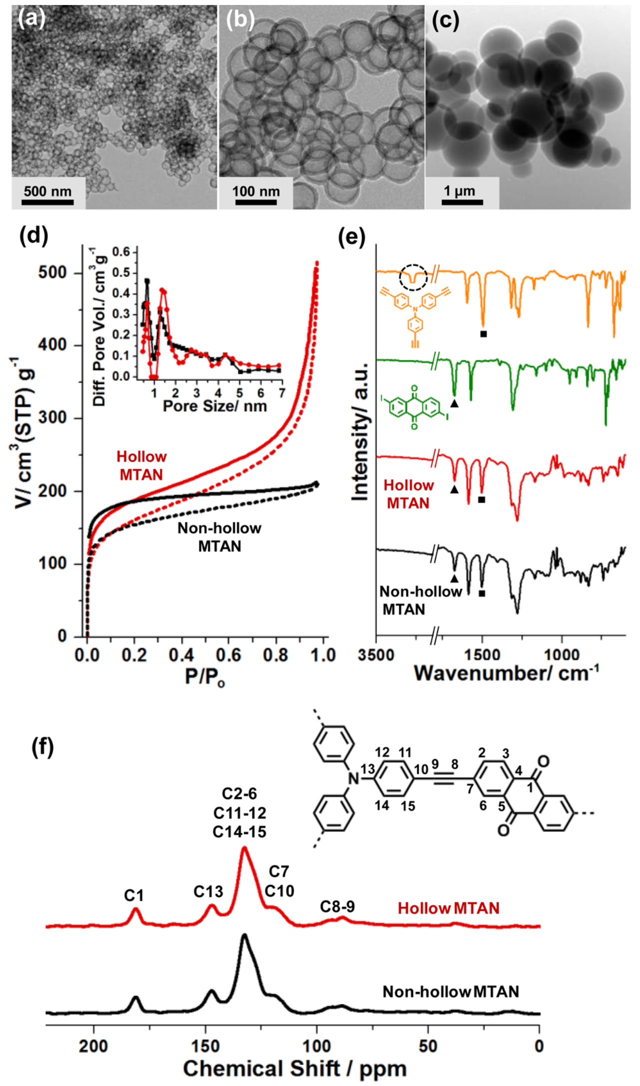


Figure 1. TEM images of hollow (a, b) and nonhollow (c) **MTAN**s, N_2 adsorption (dotted line)-desorption (solid line) isotherms (d) at 77 K, pore size distribution diagrams based on the DFT method (inset), (e) IR spectra, and (f) solid phase ^{13}C NMR spectra of hollow and nonhollow **MTAN**s.

Chemical composition of the **MTAN**s was studied by various methods. The infrared (IR) absorption spectroscopy clearly supported the coexistence of triphenylamine and anthraquinone moieties in the **MTAN**s (Figure 1e). The carbonyl peaks from the anthraquinone moieties were observed at 1677 cm^{-1}.[10] The terminal alkyne peak at 3266 cm^{-1} of the tris(4-ethynylphenyl)amine building block (indicated by dotted circle in Figure 1e)[10] disappeared through the networking. The solid phase ^{13}C NMR spectroscopy showed the carbonyl peak from anthraquinones at 181 ppm and internal alkyne peaks from triphenylamine building blocks in the range of 88−90 ppm, supporting the expected chemical structure. The elemental analysis showed 1.7 (2.35 wt % N) and 1.9 mmol/g (2.64 wt % N) of triphenylamine moieties for hollow and nonhollow **MTAN**s, respectively.

The optical properties of the **MTAN** materials were studied. Tris(4-ethynylphenyl)amine building block has a pale yellow color and thus is not efficient in the absorption of visible light. After connecting to the anthraquinone building block, the hollow **MTAN** materials have a reddish color with the maximum absorption and emission at 504 and 620 nm (excitation at 504 nm) in toluene, respectively (Figure 2a). In DMF solution, the hollow **MTAN** materials showed the maximum absorption at 507 nm, and the emission was not observed, indicating that polar solvent enhances the photoinduced intramolecular charge transfer and induces emission quenching[11] (Figure 2b). The similar trend was observed for the model compound (**M**) which was prepared by the Sonogashira coupling of (4-ethynylphenyl)diphenylamine and 2,6-diiodo-9,10-anthraquinone (Figures 2a,b).

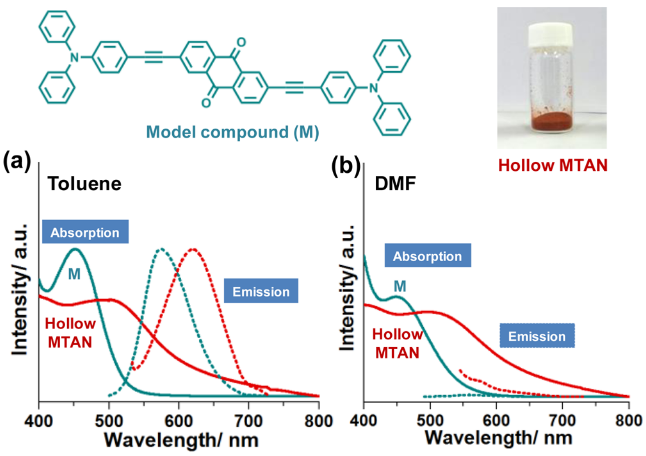
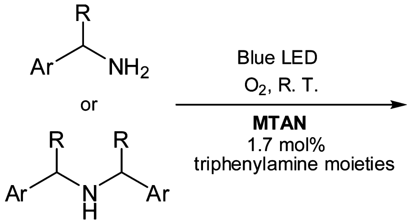


Figure 2. Absorption (solid line) and emission (dotted line) properties of hollow **MTAN**s and model compound (**M**) in toluene (a) and DMF (b). Excitation at 504 nm (toluene) and 507 nm (DMF) for the hollow **MTAN**s and 452 nm for **M** (toluene and DMF).

Recently, various methodologies for visible light-induced oxidative coupling of benzylamine to imine have been reported.[6e,8a,12] Although a significant number of organic or inorganic photocatalytic systems have been reported, the systems working at room temperature are relatively rare.[6e,8a] Considering the visible light absorption properties, the photochemical activities of the **MTAN**s were studied in visible light driven oxidative coupling of benzylamines at room temperature. Table 1 summarizes the results.

The hollow **MTAN**s showed very efficient photochemical conversion of benzylamine to imine. In our recent report,[6e] the heterogeneous system using microporous organic networks bearing benzodifuran moieties showed 96% conversion of

Table 1. Visible Light Driven Oxidative Coupling of Amines by MTANs[a]



entry	amine	solvent	time (h)	yield[b] (%)
1	benzylamine	toluene	8	59
2	benzylamine	toluene	12	75
3	benzylamine	toluene	24	99 (95)
4[c]	benzylamine	toluene	24	100
5[d]	benzylamine	toluene	24	8
6[e]	benzylamine	toluene	24	15
7[f]	benzylamine	toluene	24	29
8[g]	benzylamine	toluene	12	78
9[h]	benzylamine	toluene	12	76
10	benzylamine	DMF	12	56
11	benzylamine	DMSO	12	43
12	(4-chlorophenyl)methanamine	toluene	24	93 (91)
13	(*p*-tolyl)methanamine	toluene	24	99 (91)
14	(4-methoxyphenyl)methanamine	toluene	24	97 (95)
15[c]	(4-methoxyphenyl)methanamine	toluene	24	82
16	(3,5-dibutoxylphenyl)methanamine	toluene	24	98 (92)
17[c]	(3,5-dibutoxylphenyl)methanamine	toluene	24	31
18	(2-thienyl)methanamine	toluene	24	99 (93)
19	1-phenylethanamine	toluene	24	64 (62)
20	dibenzylamine	toluene	24	62 (55)

[a] Reaction conditions: hollow **MTANs** (10 mg, 1.7 mol % triphenylamine moieties, 1.7 mmol N/g), amine (1.0 mmol), 1 atm O_2, 3.0 mL solvent, blue LED irradiation (emission λ_{max} 460 nm, 0.8 mW/cm^2), room temperature. [b] Conversion yields by ^{1}H NMR analysis (isolated yields in parentheses). [c] Nonhollow **MTANs** (1.7 mol % triphenylamine moieties) was used. [d] No catalyst was used under blue LED irradiation. [e] Glassware was covered with Al foil under blue LED irradiation. [f] Argon was charged instead of oxygen. [g] Hollow **MTANs** recovered from entry 2 was used. [h] Hollow **MTANs** recovered from entry 8 was used.

benzylamine after 40 h at room temperature with 8 mol % benzodifuran. In comparison, the hollow **MTANs** showed 99% conversion after 24 h with 1.7 mol % triphenylamine species[13] (entries 1−3 in Table 1). The enhanced activity of the hollow **MTANs** can be attributed to the effective overlap of the absorption band with the emission band of the blue LED irradiation (maximum emission at 460 nm). Without catalyst, light, or oxygen, the hollow **MTANs** showed poor conversion, supporting the chemical transformation mainly occurred by the photochemical reaction[14] (entries 5−7 in Table 1). In polar solvents such as DMF and DMSO, the conversion was relatively poor (entries 10−11 in Table 1). For the photochemical conversion of benzylamine to imine, two main mechanisms, singlet oxygen pathway and electron transfer pathway, have been suggested in the literature[6e,8a,12] (Figure S2 in the SI). Although both pathways can simultaneously occur, at least, the dominant generation of the singlet oxygen species in toluene, compared to the system in DMF, was directly characterized by the emission spectroscopy for the singlet oxygen (Figure S3 in the SI). To investigate the recyclability, the hollow **MTANs** were separated from the reaction mixture after 12 h with 75% conversion of benzylamine. As shown in entries 2 and 8−9 in Table 1, the hollow **MTANs** maintained the activities (75−78% conversion) in three runs and the hollow morphology (Figure S4 in the SI). The hollow **MTANs** showed the good activities toward functionalized benzylamines and (2-thienyl)methanamine (entries 12−14, 16, and 18 in Table 1). The 1-phenylethanamine or dibenzylamine showed relatively poor conversion because of steric effects (entries 19 and 20 in Table 1).

The most intriguing result was the activity comparison of the hollow and nonhollow **MTANs** (Figure 3 and entries 3, 4, 14, 15, 16, and 17 in Table 1).

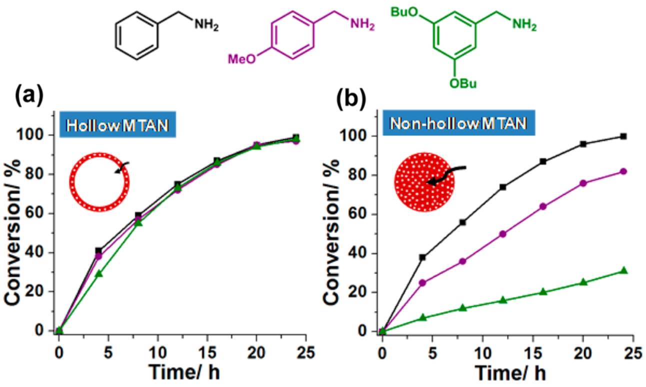


Figure 3. Visible light-driven photochemical oxidative coupling of benzylamines (1.0 mmol) by (a) hollow and (b) nonhollow **MTAN** (1.7 mol % triphenylamine moiety) under blue LED irradiation at 1 atm O_2: benzylamine, black line; (4-methoxyphenyl)methanamine, violet line; (3,5-dibutoxyphenyl)methanamine, green line.

As shown in Figure 3a, the hollow **MTANs** showed very similar activities toward benzylamine, (4-methoxyphenyl)-methanamine, and (3,5-dibutoxyphenyl)methanamine. In comparison, the nonhollow **MTANs** showed a clear difference in the activities toward these substrates (Figure 3b). As the bulkiness of substrates increased, the conversion rates significantly decreased. Recently, we and other groups suggested that the microporosity (pore size < 2 nm) of the MON materials can be changed via swelling in solvent,[3b,7d,15] and relatively big substrates (2−5 nm) can penetrate through MON materials.[7d] However, as the diffusion pathway increases, the conversion of substrates may become significantly slow for the bulkier substrates. Comparatively, in the hollow systems with a shorter diffusion pathway, this effect can be less significant. These observations indicate that the structural shape engineering of MON materials can be a significant factor in the development of catalytic systems.

In conclusion, this study shows that the networking of triphenylamine and anthraquinone can result in visible light absorbing microporous materials. The resultant **MTANs** showed activities in visible light-driven oxidative coupling of benzylamines. The activities toward bulkier substrates were more dependent on the structural shape of the **MTANs**, which can be understood by the diffusion pathway effect. We believe that more various hollow heterogeneous catalysts can be developed based on the synthetic strategy in this work.

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■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure, characterization of new compounds, PXRD pattern of hollow and nonhollow **MTAN**s, summary of mechanism, singlet oxygen detection by emission spectroscopy, and TEM images of recovered hollow **MTAN**s. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00323.

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Notes

The authors declare no competing financial interest.

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