Porous Organic Materials

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Tandem Synthesis of Photoactive Benzodifuran Moieties in the Formation of Microporous Organic Networks**

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Over the last decade, microporous organic materials have been extensively prepared through various coupling reactions.[1] In the early stages, relatively simple aromatic building blocks were used to prepare microporous organic networks (MONs) and relevant studies have focused on their physisorption behavior toward gas guests. Recently, more specific functionalities were achieved by the introduction of designed active sites into MONs.[2] Usually, the active sites could be introduced by using the predesigned building blocks or by postmodification[3] of the porous materials. If the active sites could be concomitantly formed in the network formation process for porous materials, this synthetic process would be very efficient and ideal for functional materials.[4] For example, we have demonstrated the successful incorporation of active N-heterocyclic carbene metal species into metal–organic frameworks (MOFs) during self-assembly processes.[4a–c] However, this kind of synthetic approach is relatively rare, especially in the synthesis of MONs.[4d]

Benzodifurans (BDFs) are very interesting materials owing to their unique optical and electrical properties.[5] Their electron-rich nature has enabled them to be applied as redox-active hole transfer materials in organic light-emitting devices.[5a] Moreover, very recently, *anti*-benzodifuran-based organic materials have attracted significant attention as photo- and redox-active materials in solar cells and organic field-effect transistors.[5b] *anti*-Benzodifurans can be prepared in the intramolecular cyclization reaction of 1,4-hydroquinone with two alkyne groups at the 2,5-positions.

Generally, tandem reactions in organic synthesis can be defined as a consecutive series of intramolecular reactions.[6] In well-designed tandem processes, the functional groups for the following successive reactions can be generated in situ as a result of the previous reaction. Through the introduction of tandem processes to organic synthesis, the synthetic strategies become more atom-economical, because the work-up and isolation processes for intermediates can be reduced. Thus, much effort has been made for the development of smart tandem processes for complicated target organic materials.[6]

The Cooper research group and others have shown that MONs can be prepared by Sonogashira coupling between multialkyne connectors and multihalo arene building blocks.[2e,h,7,8] We have continued to develop functional MONs.[8] We speculated that the generation of benzodifuran species can be induced in a tandem manner during the formation of the MON through a Sonogashira coupling. As far as we are aware, tandem synthetic strategies for the preparation of functional MONs have not been reported. Herein, we report the preparation of photoactive MONs with benzodifuran moieties through tandem synthetic processes, and their applications to photocatalytic coupling of primary amines.

Figure 1 shows the synthetic strategy for the synthesis of a MON containing benzodifuran moieties (BDF-MON).

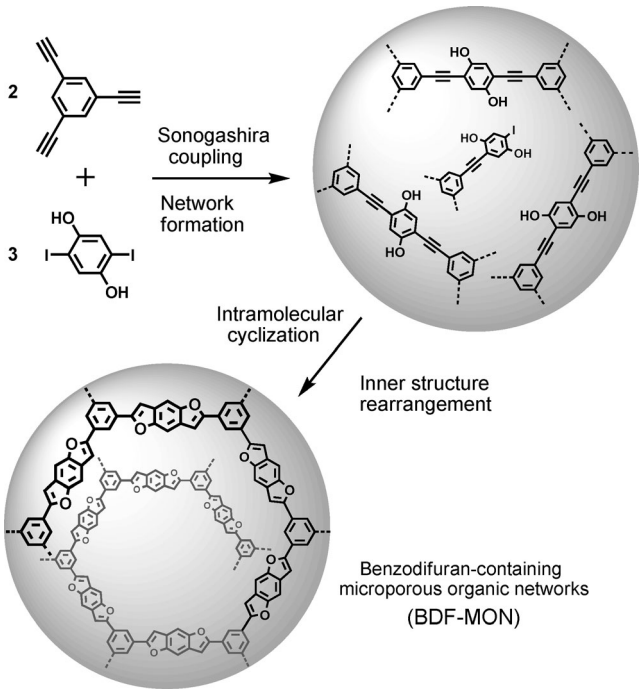

Figure 1. Strategy for the synthesis of microporous organic networks containing benzodifuran moieties.

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First, 1,3,5-triethynylbenzene was prepared by using a reported method.[9] 2,5-Diiodo-1,4-hydroquinone was prepared by iodization of 1,4-dimethoxybenzene and demethylation.[10] Then, a 2:3 stoichiometric mixture of 1,3,5-triethynylbenzene and 2,5-diiodo-1,4-hydroquinone was treated under conventional Sonogashira coupling conditions using diisopropylamine as a base (see the experimental section in the Supporting Information).[11]

During the first 30 min, a significant amount of yellow precipitates gradually appeared. The reaction mixture was further stirred for 48 h. The resultant dark-yellow precipitates were isolated by centrifugation and washed with methanol, acetone, methylene chloride, and ether. To characterize the chemical reactions in the formation of MONs, the precipitates obtained after 30 min, 2 h, 12 h, and 48 h were analyzed by using solid-state ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the precipitates obtained after 30 min showed peaks of internal alkynes at 89 and 96 ppm (asterisks in Figure 2a,b). After 2 h, the intensities of the peaks gradually decreased and a new peak appeared at 104 ppm (Figure 2c). The intensity of the peak at 104 pm gradually increased during further reaction and reached a maximum after 12 h (Figure 2d). The peaks of the aromatic parts also changed during the reaction. After 48 h, a completely different ^{13}C NMR spectrum was obtained, when compared with that of precipitates obtained after 30 min (Figure 2f). Fourier-transform infrared (FTIR) spectroscopy of the materials obtained after 30 min, 2 h, 12 h, and 48 h showed the gradual disappearance of the absorption peak at 3300–3600 cm^{-1} from the hydroxy groups (Figure S1 in the Supporting Information). A comparison with model compounds (Figure 2b,g)[5a] confirmed that the changes in the solid-state ^{13}C NMR spectra resulted from the intramolecular cyclization of the 2,5-dialkynyl-1,4-hydroquinone moieties formed in the Sonogashira coupling (Figure 1). All peaks, including that at 104 ppm, matched well with the suggested structure of benzodifuran moieties (Figure 2f and g).

When the precipitates isolated after 30 min were further treated with diisopropylamine at 90 °C for 47.5 h, the same intramolecular cyclization was observed, which was verified by ^{13}C NMR spectroscopy (Figure 2e). This observation implies that the intramolecular cyclization to benzodifurans was triggered by the base-induced addition of phenoxide to adjacent alkynes. Notably, a base-induced formation of *anti*-benzodifurans from 2,5-dialkynyl-1,4-hydroquinones was recently reported.[5]

The outer shape and inner porosity of the organic materials were investigated by scanning electron microscopy (SEM) and the Brunauer–Emmett–Teller (BET) method. In the SEM images, the precipitates obtained after 30 min showed a spherical shape (Figure 3a). There were nearly no changes in the shape of the materials obtained after 2 h, 12 h, and 48 h (Figure 3b–d). In contrast, BET analysis showed dramatic time-dependent changes in the porosity of the materials (Figure 3e). The precipitates obtained after 30 min showed negligible microporosity with a surface area of 8 m^2 g^{-1}. After 2 h, 12 h, and 48 h, the BET surface area values of materials increased to 14 m^2 g^{-1}, 348 m^2 g^{-1}, and 455 m^2 g^{-1}, respectively. Microporosity with mainly 1–2 nm pore sizes was observed in precipitates obtained after 48 h. Considering these observations and the solid-state ^{13}C NMR studies, it can be speculated that after the coarse connection of building blocks to form spherical materials through the Sonogashira coupling reaction, further network formation

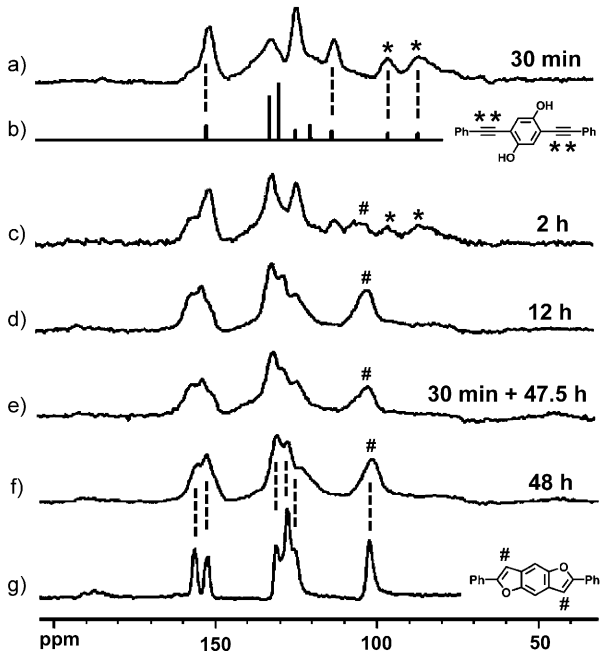


Figure 2. Solid-state ^{13}C NMR spectra of the precipitates obtained after 30 min (a), 2 h (c), 12 h (d), and 48 h (f) by reaction of 1,3,5-triethynylbenzene and 2,5-diiodo-1,4-hydroquinone under Sonogashira coupling conditions. ^{13}C NMR spectra of model compounds (b, g). e) ^{13}C NMR spectrum of precipitates that were further treated for 47.5 h in diisopropylamine solution using the materials isolated after 30 min.

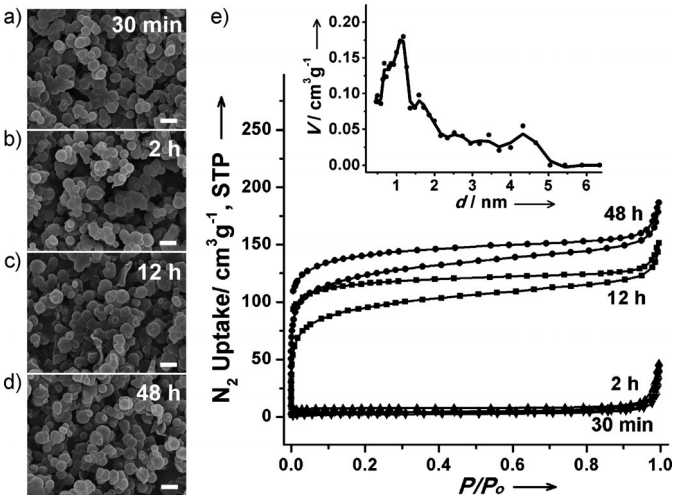


Figure 3. SEM images (a–d) and N_2 adsorption/desorption isotherms at 77 K (e) of the precipitates obtained after 30 min, 2 h, 12 h, and 48 h by reaction of 1,3,5-triethynylbenzene and 2,5-diiodo-1,4-hydroquinone under Sonogashira coupling conditions. The inset in (e) displays the DFT pore-size distribution curve (V = differential pore volume, d = pore size) of precipitates obtained after 48 h (BDF-MON). Scale bar in SEM images = 1 μm. STP = standard temperature and pressure.

and chemical transformation to benzodifuran moieties occurred concomitantly within the spheres. The network formation in the ripening period induced the inner porosity of the MONs.

According to thermogravimetric analysis, BDF-MON was stable up to approximately 286 °C (Figure S2 in the Supporting Information). Powder X-ray diffraction studies showed that BDF-MON has amorphous characteristics (Figure S3 in the Supporting Information), as generally reported for MONs prepared by the coupling reaction of organic building blocks.[7]

Recently, benzodifuran-containing organic polymers have shown promising photoelectrical performances in polymer solar cells.[5b] In these photovoltaic devices, benzodifuran moieties acted as electron donors and photosensitizers. Considering these photoredox behaviors, we examined the photocatalytic properties of BDF-MON in the oxidative conversion of primary amines. BDF-MON showed a significant absorption in the visible-light region of 400–500 nm and emission at 430–700 nm (Figure 4a). In the literature, it was interpreted that the absorption originates from the π–π* transition of benzodifuran moieties and pending side-conjugated arenes.[5c] It was reported that the photoactive aromatic supramolecules can mediate electron transfer from 1,4-bis(dimethylamino)benzene to oxygen, thereby resulting in the generation of a blue-colored cationic radical species.[12] BDF-MON mediated the abstraction of an electron from 1,4-bis(dimethylamino)benzene to form the blue-colored species with strong absorption peaks at 565 nm and 614 nm under irradiation with a blue LED (Figure 4b and see the Supporting Information for the detailed experimental procedure). Thus, we investigated the photocatalytic transformation of amines (electron donor) by using a catalytic amount of BDF-MON under irradiation with a blue LED.

Visible-light-induced photocatalytic systems for the oxidative conversion of primary amines into imines have been reported very recently.[13] However, the reaction temperatures were relatively high (ca. 80 °C).[13c–d] Catalytic systems working at room temperature are relatively rare.[13a] Herein, we conducted photocatalytic studies of BDF-MON with benzylamine under 1 atm oxygen at room temperature (Table 1).

After 20 h and 40 h under irradiation with a blue LED a catalytic amount (8 mol% of BDF moieties to amines) of BDF-MON resulted in 62% and 97% conversion of benzylamine into the imine, respectively (entries 1,2 in Table 1). After the reaction, BDF-MON was retrieved by centrifugation. The resultant solution was colorless and transparent, which implies that the reaction proceeded in a heterogeneous

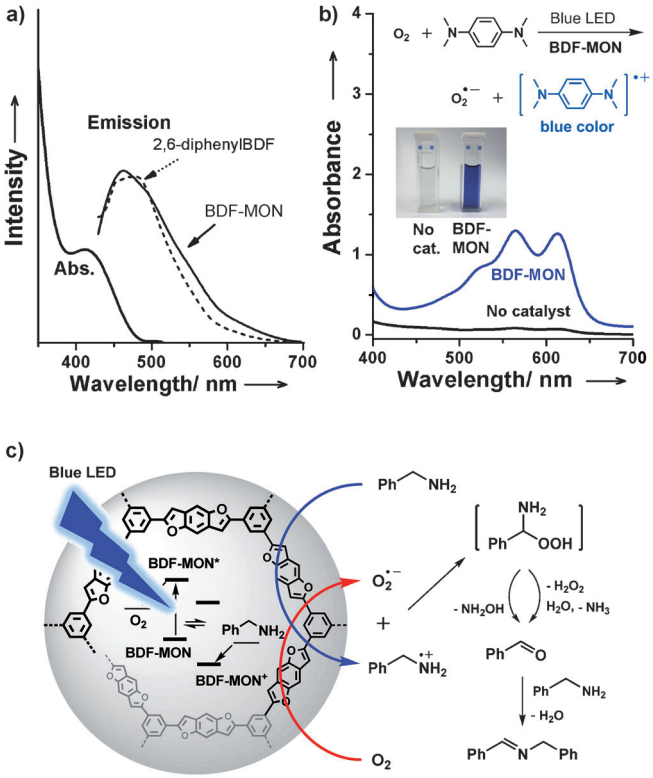
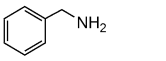
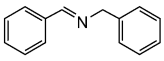
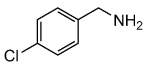
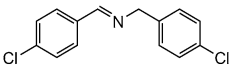
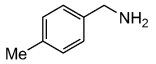
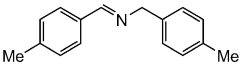
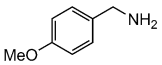
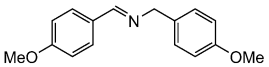
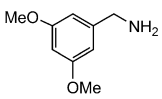
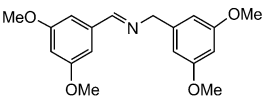
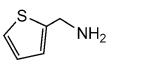
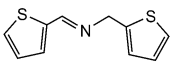
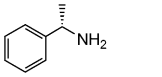
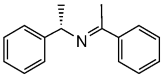
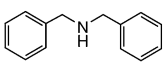
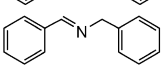


Figure 4. a) UV/Vis absorption and emission spectra (exc. 410 nm) of BDF-MON and emission spectrum of 2,6-diphenylbenzodifuran. The emission from medium (CH_3CN) was calibrated. b) UV/Vis absorption spectra and photograph of the cationic radical species of 1,4-bis(dimethylamino)benzene (100 mM in 3 mL CH_3CN) generated by BDF-MON (21 mg) and irradiation with a blue LED for 1 h in the presence of oxygen. c) A suggested photocatalytic process of oxidative conversion of benzylamine into imine by BDF-MON under irradiation with a blue LED.[17]

Table 1: Photocatalytic oxidative conversion of amines into imines by BDF-MON.[a]

Entry	Amine	Product	Yield [%][b]
1[c]			62(57)
2			97(89)
3[d]			96(93)
4[e]			8
5[f]			4
6			97(92)
7			96(91)
8			93(87)
9			95(91)
10			98(91)
11			35(29)
12			61(54)

[a] Reaction conditions: amine (1.0 mmol), O_2 (1 atm), cat. BDF-MON (21 mg, 8 mol% benzodifuran moieties to amines based on elemental analysis), CH_3CN (3.0 mL), 40 h, room temperature. [b] Determined by ^1H NMR spectroscopic analysis (yields of isolated products in parenthesis). [c] Reaction time 20 h. [d] The recovered catalysts were used. [e] Glassware was covered with Al foil under irradiation with a blue LED. [f] No BDF-MON used under irradiation with a blue LED.

manner. The recovered BDF-MON showed nearly no change in the SEM image (Figure S4 in the Supporting Information), and maintained catalytic activity with 96% conversion of benzylamine after 40 h (entry 3 in Table 1). In a control experiment, with the glassware completely covered by aluminum foil, the catalytic systems with BDF-MON showed 8% conversion of benzylamine for 40 h at room temperature under irradiation with a blue LED, thus confirming that the chemical transformation was triggered by photoirradiation (entry 4 in Table 1). Moreover, when the reaction mixture was irradiated by a blue LED without BDF-MON, only 4% conversion of benzylamine was observed after 40 h, thus supporting that BDF-MON mediated the oxidative conversion of benzylamine (entry 5 in Table 1). The model compound, 2,6-diphenylbenzodifuran showed 29% conversion of benzylamine after 40 h under irradiation with a blue LED, possibly owing to its blue-shifted absorption band.

Next, various substrates were screened in the optimized catalytic system. The influence of the functional groups on the phenyl ring of benzylamine was not significant (entries 6–9 in Table 1). 2-Thienylmethylamine showed excellent conversion (98%, entry 10 in Table 1). However, the methyl substituent at the methylene group of benzylamine significantly retarded the conversion (35%, entry 11 in Table 1). Interestingly, *N*,*N*-dibenzylamine, known as a better substrate in conventional oxidative imination,[13a,14] showed less conversion than benzylamine, possibly owing to steric hindrance (entry 12 in Table 1).

Recently, two main photocatalytic reaction mechanisms, known as the photoredox process[13,15] or the singlet-oxygen ($^1O_2$) pathway,[14,16] have been suggested for the photooxidation of benzylamine. The former consists of 1) photoinduced generation of an $O_2^{\bullet-}$ radical and a benzylamine cationic radical through electron transfer, 2) the formation of benzaldehyde or phenylmethanimine ($PhCHNH_2$), and 3) the successive reaction of additional benzylamine with these species (Figure 4c).[13] In comparison, the singlet-oxygen pathway is based on energy transfer from the excited triplet state (with long lifetimes, >1 μs) of photosensitizers to triplet oxygen molecules.[16,2h] The reaction pathway is dependent on the properties of photosensitizers. In this study, the lifetime of BDF-MON emission was relatively short (at least shorter than 5 ns, Figure S5 in the Supporting Information). Moreover, the typical long-lived emission at 1268 nm from singlet oxygen[15] was not detected in straightforward photophysical studies on the irradiated BDF-MON and oxygen (Figure S6 in the Supporting Information). The irradiation of 1,4-bis(dimethylamino)benzene under oxygen in the presence of BDF-MON resulted in a color change to blue (Figure 4b), implying electron transfer from amine to oxygen mediated by BDF-MON.[12]

To further rationalize the photoredox process of BDF-MON, density functional theory (DFT) calculations were conducted for the simplified BDF-MON (Figures S7–S10 in the Supporting Information). The LUMO of the model components of BDF-MON was higher than that of oxygen. The HOMO of benzylamine was higher than the SOMO of the oxidized model component of BDF-MON. Thus, the photoredox pathway for oxidative conversion of benzylamine by BDF-MON is quite reasonable and may behave according to the oxidative quenching process.[15] Considering this and the detection of benzaldehyde derivatives[13b] as intermediates by ^1H NMR spectroscopy (Figure S11 in the Supporting Information), the reaction mechanism shown in Figure 4c and Figure S8 in the Supporting Information is suggested.[17]

This work shows that a tandem synthetic strategy can be successfully applied to introduce active species into MONs. We believe that more diverse tandem synthetic approaches for functional MONs can be designed by the delicate combination of network-forming reactions for MONs, and intramolecular transformation for the generation of functional species within MONs.

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