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Covalent Organic Frameworks

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Three-Dimensional Radical Covalent Organic Frameworks as Highly Efficient and Stable Catalysts for Selective Oxidation of Alcohols

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***Abstract:** With excellent designability, large accessible inner surface, and high chemical stability, covalent organic frameworks (COFs) are promising candidates as metal-free heterogeneous catalysts. Here, we report two 3D radical-based COFs (JUC-565 and JUC-566) in which radical moieties (TEMPO) are uniformly decorated on the channel walls via a bottom-up approach. Based on grafted functional groups and suitable regular channels, these materials open up the application of COFs as highly efficient and selective metal-free redox catalysts in aerobic oxidation of alcohols to relevant aldehydes or ketones with outstanding turn over frequency (TOF) up to 132* h^{-1}*, which has exceeded other TEMPO-modified catalytic materials tested under similar conditions. These stable COF-based catalysts could be easily recovered and reused for multiple runs. This study promotes potential applications of 3D functional COFs anchored with stable radicals in organic synthesis and material science.*

Covalent organic frameworks (COFs),[1] an emerging class of crystalline porous organic materials, are considered as prospective platforms for heterogeneous chemical catalysis, owning to their highly designable organic skeletons, abundant open active sites, and excellent chemical stability. After the first report of COF-based catalyst (Pd/COF-LZU1) by Wang and co-workers in 2011,[2a] some related works have been prepared.[2] For example, we have recently developed a series of three-dimensional (3D) COF-based catalysts by the functional design,[3] including 3D base-functionalized COFs for highly selective catalysis in Knoevenagel condensation reactions,[3a] 3D COFs with dual linkages as bifunctional catalysts for one-pot cascade reactions,[3b] and 3D metal-containing Salphen COFs as catalytic antioxidants for the removal of superoxide radicals.[3c] Often the catalytically active components (such as metal ions and nanoparticles) of a large portion of COF catalysts are incorporated through weak interaction, resulting in potential leaching or aggregation during catalytic procedures, which limits the stability and reusability of these materials. Recently, bare COF skeletons as metal-free heterogeneous chemical catalysts have attracted broad interests because their active sites were covalently bound to the backbone.[2i] Among these materials, strong covalent bonds promise high chemical stability and excellent reusability while the exposed organic functional groups serve as catalytic centers. However, the development of such COF-based catalysts still remains a great challenge.

The stable organic nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO), have been widely studied as highly efficient metal-free redox catalysts.[4] Individual TEMPO molecules and their derivatives have been employed in a broad range of chemical transformations, but the recovery and reuse of catalysts are highly desirable since TEMPO is considerably expensive. As a result, various supporting materials have been attempted for the immobilization of TEMPO, such as silica, amorphous polymers, and metal-organic frameworks (MOFs).[5] However, it was still difficult to prepare catalysts combining excellent recyclability and high catalytic activity due to irregular pores or poor stability in traditional supporting materials. We considered COFs a promising candidate for TEMPO immobilization, which can lead to excellent redox catalysis due to their large exposed inner surface, uniform nano-channels, highly designable structures, and good chemical stability. Nevertheless, only a few reports of TEMPO-decorated COFs were available up to date,[6] and they were limited to post-modified 2D frameworks, which has extremely restricted their performances.

Herein, we report two 3D TEMPO-based COFs via a bottom-up strategy, termed JUC-565 and JUC-566 (JUC = Jilin University China). Different from previously reported 2D TEMPO-based COFs, TEMPO groups as radical moieties were uniformly anchored to the channel walls of these 3D COFs with high density. Since the whole framework was

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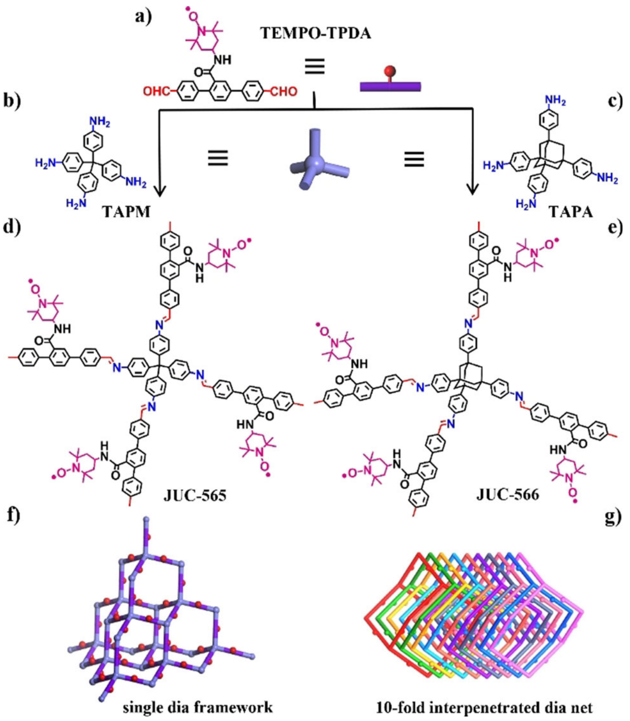
connected via strong covalent bonds, these materials showed high chemical stability in strong basic or acidic aqueous solutions. These functional COFs have been demonstrated to be highly selective and reusable metal-free redox catalysts for the application in aerobic oxidation of alcohols to relevant aldehydes or ketones with remarkable turn over frequency (TOF) as high as 132 h^{-1}, which is the highest ever reported under similar conditions. To the best of our knowledge, this study represents the first case of 3D functional COFs decorated by TEMPO radicals and their application as metal-free redox catalysts for aerobic oxidation of alcohols.

The synthesis of 3D radical-based COFs was carried out by solvothermal condensation of TEMPO-TPDA (TPDA = [1,1′:4′,1′′-terphenyl]-4,4′′-dicarbaldehyde), and tetra(4-aminophenyl)methane (TAPM) or 1,3,5,7-tetrakis(4-aminophenyl)adamantane (TAPA) in a mixture of dioxane, mesitylene, and acetic acid at 120 °C for 3 days (Scheme 1). A variety of methods have been utilized for structural confirmation. Scanning electron microscopy (SEM, Figures S1 and S2) images revealed isometric nanocrystals building random aggregates for both COFs. Fourier transform infrared (FT-IR) spectra showed new peaks at 1658 cm^{-1} for both COFs, which is characteristic of the imine bond. At the same time, almost complete disappearance of C=O (1696 cm^{-1} for TEMPO-TPDA) and N−H stretching (ca. 3394 cm^{-1} for TAPM and ca. 3332 cm^{-1} for TAPA) proved the transformation of aldehyde and amine groups (Figures S3 and S4). Furthermore, thermogravimetric analysis (TGA) illustrated good thermal stability (ca. 300 °C under N_2) of 3D radical-based COFs (Figures S5 and S6). Outstanding chemical stability was also verified by their retained powder X-ray diffraction (PXRD) patterns after immersing in different organic solvents and strong basic (1 M NaOH) or acidic (1 M HCl) aqueous solutions for one week (Figures S7–10). Moreover, the radical feature probed by electron paramagnetic resonance (EPR) spectroscopy at room temperature showed peaks at $g = 2.0096$ for JUC-565 and 2.0097 for JUC-566 respectively, which is well consistent with that of TEMPO radical ($g = 2.0097$, Figures S12–14).

The crystalline structures were verified by the PXRD and structural simulations (Figure 1). After a geometrical energy minimization by the Materials Studio software package[7] based on 10-fold interpenetrated **dia** nets and disordered pendant functional groups,[8] their unit cell parameters were acquired ($a = b = 28.838$ Å, $c = 7.1132$ Å and $\alpha = \beta = \gamma = 90°$ for JUC-565; $a = b = 31.438$ Å, $c = 7.6704$ Å and $\alpha = \beta = \gamma = 90°$ for JUC-566; Tables S2 and S3). The simulated PXRD patterns were in good agreement with the experimental ones. Moreover, the experimental PXRD patterns were analyzed by full profile pattern matching (Pawley) refinements. Peaks at 4.31, 6.14, 6.76, 8.68, 9.77 and 13.15° for JUC-565 belong to the (110), (200), (210), (220), (310), and (330) Bragg peaks of space group $P\bar{4}$ (No. 81); peaks at 3.97, 5.70, 6.39, 8.05, 9.01 and 12.54° for JUC-566 correspond to the (110), (200), (210), (220), (310), and (330) Bragg peaks of the space group $P\bar{4}$ (No. 81). The calculated results were consistent with the measured ones with good agreement factors ($Rp = 1.15\%$ and $\omega Rp = 1.65\%$ for JUC-565; $Rp = 0.73\%$ and $\omega Rp = 1.09\%$



Scheme 1. Strategy for constructing 3D radical-based COFs. Molecular structures of TEMPO-TPDA (a) as a linear 2-connected building unit as well as TAPM (b) or TAPA (c) as a tetrahedral 4-connected building unit. Two novel 3D radical-based COFs, JUC-565 (d) and JUC-566 (e), prepared by the condensation reaction of TEMPO-TPDA and TAPM or TAPA. A single **dia** framework (f) and 10-fold interpenetrated **dia** net (g) in 3D radical-based COFs.

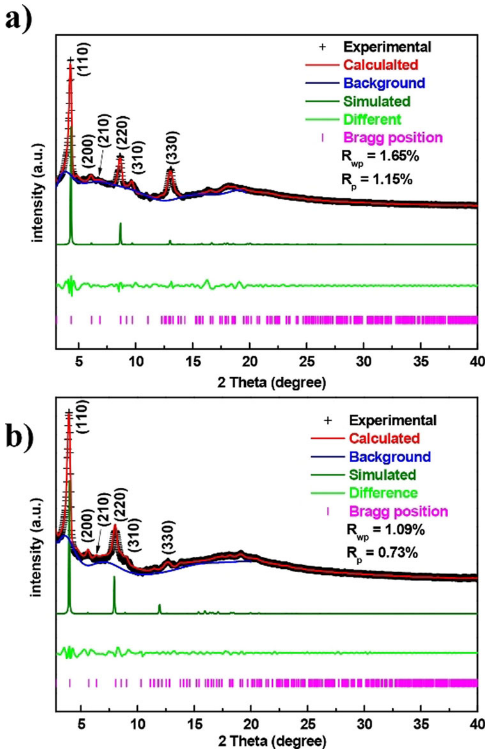


Figure 1. PXRD patterns of JUC-565 (a) and JUC-566 (b).

for JUC-566). Furthermore, we tried alternative structures with 9- or 11-fold interpenetrated **dia** topology; however, there were apparent differences between the simulated and experimental PXRDs (Figures S15–22). Also, the PXRD pattern of JUC-565 was in good agreement with that of LZU-79 with an approximate length of linkers and 10-fold interpenetrated **dia** net, which has been proved by its single-crystal X-ray diffraction (Figure S23).[9] In terms of these results, the obtained COFs are proposed to be the expected architectures possessing microporous channels (ca. 0.8 nm for JUC-565 and ca. 0.9 nm for JUC-566), which are uniformly decorated by TEMPO radicals (Figure 2 and Figure S24).

The porosity and specific surface areas of 3D radical-based COFs were determined by N_2 adsorption measurements at 77 K. As shown in Figure 3, both COFs exhibited sharp gas uptake at low relative pressure (below 0.1 P/P_0), which reveals their microporous nature. An inclination of the isotherm in the 0.8–1.0 P/P_0 range and slight desorption hysteresis can be observed due to the presence of textural mesopores.[10] The Brunauer–Emmett–Teller (BET) surface areas were calculated to be 313 $m^2 g^{-1}$ for JUC-565 and 482 $m^2 g^{-1}$ for JUC-566 (Figures S25 and S26), which are much higher than those from 2D radical-based COFs, that is, only 5.2 $m^2 g^{-1}$ for $[TEMPO]_{100\%}$-NiP-COF[6a] and 34 $m^2 g^{-1}$ for T-COF-100.[6b] The nonlocal density functional theory (NLDFT) was utilized to estimate their pore size distributions. JUC-565 and JUC-566 demonstrated microporous cavities with ca. 0.9 nm and ca. 1.0 nm, respectively (Figure 3, inset), which are in good agreement with pore sizes predicted from their crystal structures.

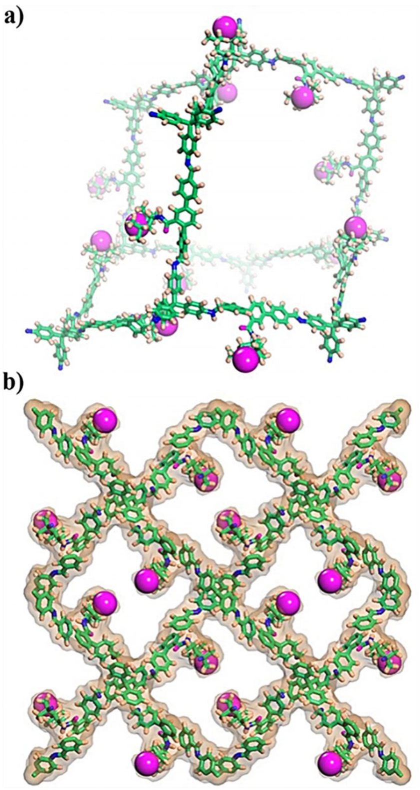


Figure 2. Extended structure of JUC-565: a) single **dia** network and b) 3D porous framework viewed along the c axis. The pink balls represent TEMPO radicals. C green, H yellow, N blue, O pink.

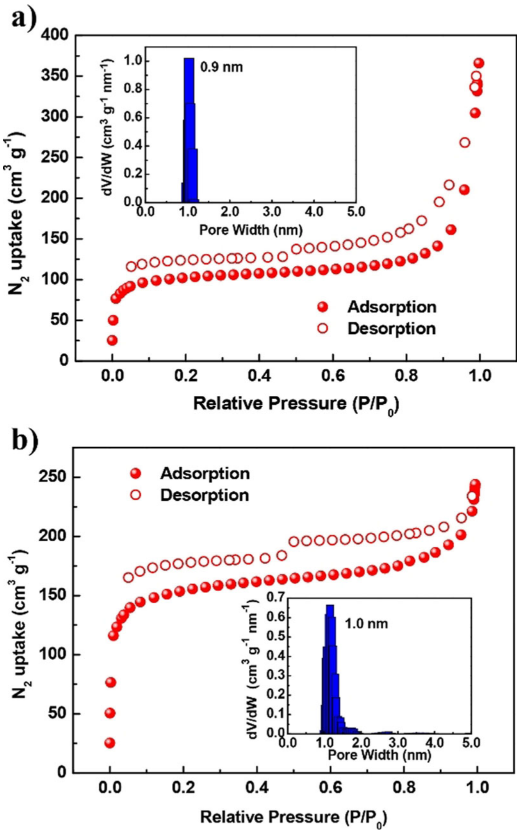
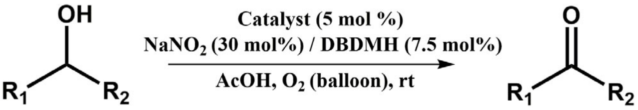


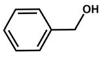
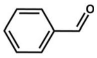
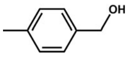
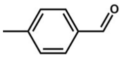
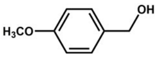
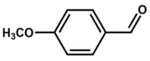
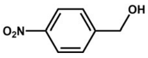
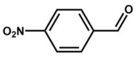
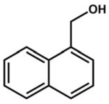
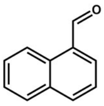
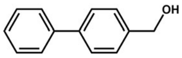
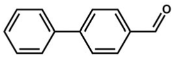
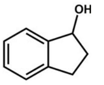
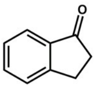
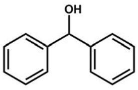
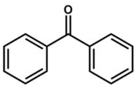
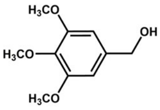
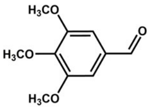
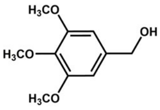
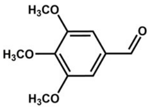
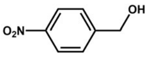
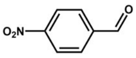
Figure 3. N_2 adsorption–desorption isotherms at 77 K for JUC-565 (a) and JUC-566 (b). Inset: pore-size distribution calculated by fitting on the NLDFT model to the adsorption data.

Encouraged by the abundant TEMPO radicals, good chemical stability, high surface areas and suitable regular pores of 3D radical-based COFs, JUC-566 was chosen to evaluate the catalytic performance of a metal-free heterogeneous catalyst for aerobic oxidation of hydroxyl to carbonyl. Typically, the catalytic reaction was carried out in a glass vial with the COF catalyst (5.0 mol% based on nitroxide radical), $NaNO_2$ (30.0 mol%) as dioxygen activator, 1,3-dibromo-5,5-dimethylhydantoin (DBDMH, 7.5 mol%) as co-catalyst, and anhydrous acetic acid as solvent (AcOH, 0.5 mL) under oxygen atmosphere (O_2 balloon) at room temperature.

As shown in Table 1, successful oxidation of a broad spectrum of alcohols to the corresponding carbonyl compounds with high yields was achieved. For example, the reaction of benzyl alcohol could be completed in 9 min with a 99% yield (Table 1, entry 1). Notably, its TOF was calculated as high as 132 h^{-1}, which has surpassed previous reported TEMPO-anchored materials under similar reaction conditions (Table S1), such as MOFs (19.2 h^{-1} for UiO-67-TEMPO),[11] amorphous polymers (40 h^{-1} for TEMPO-CMP-4),[12] ordered mesoporous silica (111 h^{-1} for SBA-15-ABNO),[13] oxide nanoparticles (125 h^{-1} for MNST).[14] The para-substituted benzyl alcohols could also be transformed to the corresponding aldehydes in nearly quantitative yields (Table 1, entries 2–6). Meanwhile, catalytic oxidation of

Table 1: Aerobic oxidation of alcohols using JUC-566 catalyst.[a]



Entry	Alcohol	Product	t [min]	Yield [%][b]
1			9	99
2			10	99
3			20	99
4			30	99
5			40	98
6			40	99
7			40	98
8			20	99
9			60	5
10[c]			20	99
11[d]			30	43

[a] Reaction conditions: 0.2 mmol of alcohol, 8.0 mg of JUC-566 (5.0 mol% of nitroxide radical), 4.2 mg of $NaNO_2$ (30.0 mol%), and 4.3 mg of DBDMH (7.5 mol%) in 0.5 mL of AcOH with an O_2 balloon at room temperature. [b] Determined by ^1H NMR spectroscopy. [c] Reaction conditions: the catalyst was replaced with TEMPO molecule and all other conditions remained the same. [d] Reaction conditions: the absence of DBDMH and all other conditions remained the same.

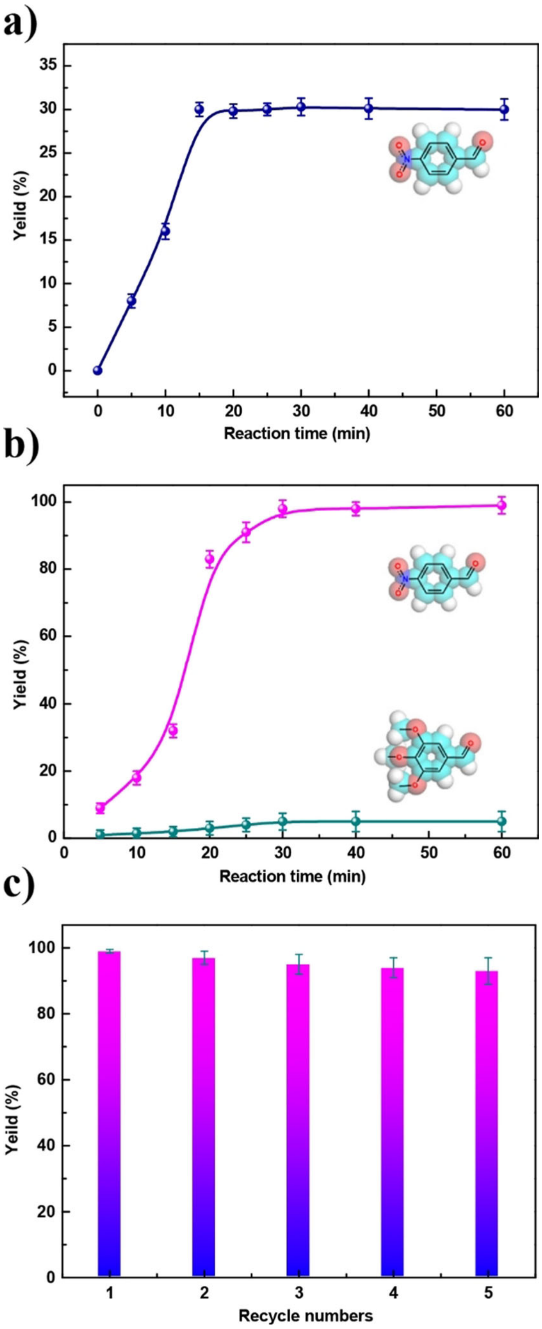


Figure 4. a) Yield vs. time curve for aerobic oxidation controlled by the addition or removal of COF crystals. b) Yield vs. time curves for aerobic oxidation with substrates of different sizes. c) Recyclability study of aerobic oxidation with 4-nitrobenzyl alcohol as the substrate.

larger substrates required longer reaction time, possibly caused by the slow diffusion through COF channels. Subsequently, the reaction was extended to some other alcohols, including secondary alcohols, which produce ketones after oxidation (Table 1, entries 7 and 8). Noteworthy, the catalytic oxidation reactions of all selected substrates showed high yields, illustrating the generality of this catalysis system. To further confirm the function of JUC-566 in the catalytic transformation, we attempted to remove it by filtration after 15 mins of reaction, and it was found that the reaction almost immediately ceased (Figure 4a), which proves the heterogeneous nature of catalytic reaction.

More importantly, thanks to the uniform channels of the frameworks, JUC-566 exhibited an amazing size selectivity. For instance, only 5% of the target product was detected even after 60 min under similar conditions for 3,4,5-trimethoxybenzyl alcohol with a molecular size of 1.0 × 1.1 nm (larger than the aperture of JUC-566 of about 0.9 nm, Table 1 entry 9 and Figure 4b). Meanwhile, a controlled experiment was performed with the catalysis of TEMPO molecules under similar conditions and 99% transformation of 3,4,5-trimethoxybenzyl alcohol was achieved in 20 mins (Table 1, entry 10). These results indicated that the catalytic reaction took place in the COF's channels and that JUC-566 possessed excellent size selectivity towards substrate dimensions. In addition, a controlled experiment without the addition of DBDMH has been also studied by using 4-nitrobenzyl alcohol as the substrate (Table 1, entry 11). The catalytic reaction could still happen without adding DBDMH, but only 43 % of the alcohol was converted into the corresponding aldehyde after 30 min, which means that DBDMH as a co-catalyst plays an important auxiliary role.[12] After that, the cycling performance of this catalyst was also investigated with 4-nitrobenzyl alcohol as the substrate. After the reaction was completed, the catalysts could be recovered by simple filtration, and used for the next run. After five cycles, a high yield of 95 % could still be observed (Figure 4c). Furthermore, the preserved PXRD pattern of the recovered JUC-566 confirmed its structural integrity after recycling tests (Figure S11).

In summary, by using a pre-designed TEMPO-based monomer, we develop two robust 3D radical-based COFs, JUC-565 and JUC-566. These materials are provided with high stability, large surface areas, suitable regular pores, and abundant accessible TEMPO moieties on the channel walls. Combining high efficiency and good reusability, JUC-566 exhibit extraordinary selective catalytic performance for aerobic oxidation of various alcohols to the corresponding aldehydes or ketones with great TOF up to 132 h^{-1}, which is much higher than those from previous reported TEMPO-decorated catalytic materials under similar conditions, including MOFs, silica, amorphous polymers, and oxide nanoparticles. These results thus open an avenue towards designing 3D functionalized COFs and promote their applications in organic synthesis and material science.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: alcohol oxidation · covalent organic frameworks · functionalization · radicals · selectivity

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Communications

Covalent Organic Frameworks

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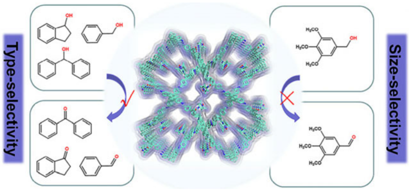
Three-Dimensional Radical Covalent Organic Frameworks as Highly Efficient and Stable Catalysts for Selective Oxidation of Alcohols



Three-dimensional covalent organic frameworks (COFs) decorated with nitroxyl radicals are successfully prepared and employed as mild, efficient, and recyclable catalysts for selective oxidation of alcohols to aldehydes or ketones.