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Fluorinated Porous Conjugated Polyporphyrins via Direct C–H Arylation Polycondensation: Preparation, Porosity, and Heterogeneous Catalyst for Baeyer–Villiger Oxidation

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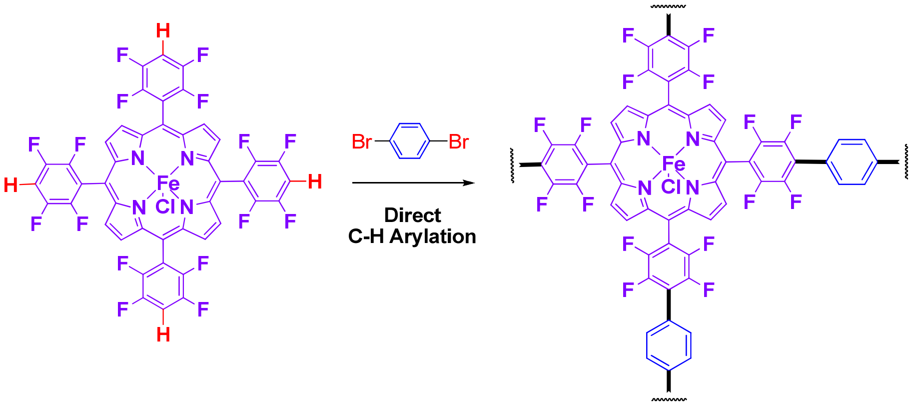
Graphic Abstract

Fluorinated Porous Conjugated Polyporphyrins via Direct C–H Arylation Polycondensation: Preparation, Porosity, and Heterogeneous Catalyst for Baeyer–Villiger Oxidation

Qiang Cao, Qing Yin, Qi Chen,* Zhi-Bing Dong,* and Bao-Hang Han*



Fluorinated Fe-porphyrin conjugated porous polymers were synthesized through direct C–H arylation polymerization and used as heterogeneous catalysts for Baeyer–Villiger oxidation.

Abstract

Considering high reactivity of fluorinated Fe-porphyrin and good stability of porphyrin-based porous polymer, fluorinated Fe-porphyrin conjugated porous polymers (**FPOP-3~6**) were synthesized through direct C–H arylation polymerization and well characterized. The obtained materials are chemically and thermally stable, in which **FPOP-3** exhibits the highest Brunauer–Emmett–Teller specific surface area (about 840 m^2 g^{-1}). For function studies of the obtained polymers as heterogeneous catalyst, catalytic transformation of cycloketones to lactone by oxygen via Baeyer–Villiger oxidation was used as a model reaction. Fluorinated phenyl substituents of the Fe-porphyrin are not only beneficial to the conversion, but also can stabilize porphyrin to restrain the catalyst breakdown. **FPOP-3** with high porosity exhibits the best catalytic efficiency and recycling effect. The recovered catalyst also shows good catalytic activities after three times recycling with small loss in yields.

Keywords: Baeyer–Villiger oxidation; direct arylation; fluorinated polymers; heterogeneous catalysis; porphyrin; porous organic polymers.

Introduction

Fe-porphyrin is an analogue of heme cofactor in kinds of cytochrome P450 enzymes with responsibilities for various biologically catalytic oxidation transformation.[1] By combining with various oxidant sources, Fe-porphyrin has been widely used as biomimetic catalyst for oxidative transformation in synthetic chemistry.[2] However, owing to production of μ-oxo dimmers or decomposion of porphyrin ring during oxidation process,[3] synthetic Fe porphyrin easily deactivated during oxidation reaction,[2] which limit its application as oxidation catalyst. Formation of Fe-porphyrin-incorporating porous polymers is reported to stabilize Fe-porphyrin catalysts in oxidation chemistry by mimicking essential features of biological systems,[4] in which the heme moiety is enveloped within a large protein structure.

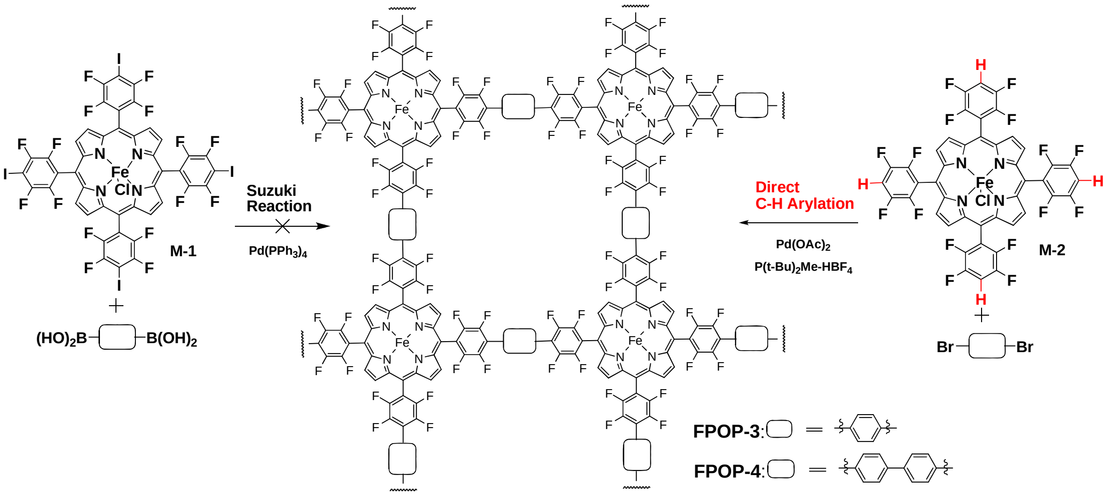
It is well known that formation of the iron oxo complex as the active species is presumably a key step during the oxidation reaction catalyzed by iron tetraarylporphyrins.[5] Ruasse's group reported that iron tetrakis-(pentafluorophenyl)porphyrin (F20TPPFe)[6] possesses a high catalytic efficiency as catalysts for the H_2O_2-induced oxidation of mustard models among a number of iron tetraarylporphyrins with different phenyl substituents in ligands. Fluorinated phenyl substituents of the Fe-porphyrin not only are beneficial to the conversion, but also can stabilize porphyrin to restrain the catalyst breakdown.

Since metalloporphyrins have facilitated a variety of crucial chemical processes such as oxygen transfer, photosynthetic reactions, and catalytically oxidative transformation, porous polymers containing porphyrins exhibit important application as heterogeneous catalysts[4,7,8,9,10] and electrocatalysts.[11] Up to now, most of porphyrin-based porous polymers are prepared by different kinds of classic C–C cross coupling polycondensation,[12,13] for example Sonogashira–Hagihara reaction, Suzuki reaction, and alkyne–alkyne homocoupling reaction. As for fluorinated Fe-porphyrin porous polymer, the related report is limited. McKeown group reported the synthesis of a microporous polymer (FeP-PIM) based on fluorinated porphyrin.[14] In this polymer, the fluorinated Fe-porphyrin moieties are coupled each other through dibenzodioxane units. Nguyen and Hupp reported a fluorinated Fe-porphyrin porous polymer obtained by polycondensation of a tetra(4-aminophenyl)methane with fluorinated bis(phthalic acid)porphyrin.[4] Modification of the polymer by metal complexing affords microporous Fe-porphyrin-containing polymer, which shows catalytic activities for epoxidation and hydroxylation.

Considering high reactivity of fluorinated Fe-porphyrin and good stability of porphyrin-based porous polymer, herein, fluorinated Fe-porphyrin conjugated porous polymers were designed and synthesized. The prepared materials with moderate Brunauer–Emmett–Teller (BET) specific surface area can be used as efficient heterogeneous catalysts in Baeyer–Villiger (BV) oxidation for transformation of different cycloketones. We believe that the fluorinated Fe-porphyrin polymers with permanent porosity, chemical and thermal stability exhibit potential use as recyclable heterogeneous catalyst for chemical transformation.

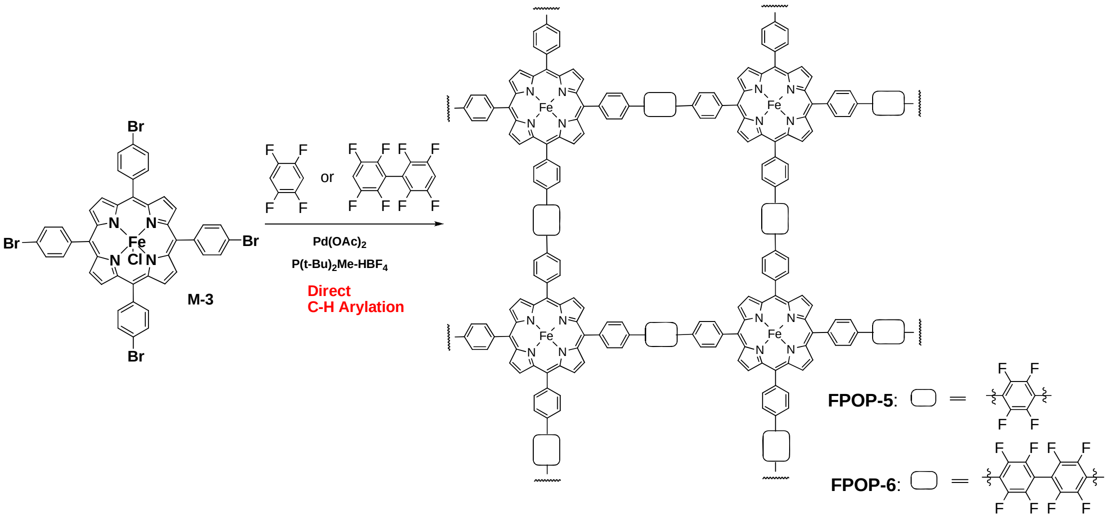
Results and Discussion

It is well-known that the Suzuki coupling reaction, as representation of transition-metal catalyzed cross-coupling reactions, is a reliable method for preparation of π-conjugated linear polymers and porous polymeric networks.[15] Various conjugated porous polymers were prepared smoothly and efficiently through Suzuki coupling polymerization.[16,17] Therefore, fluorinated porphyrin monomer **M-1** was prepared originally for the Suzuki coupling reaction with diboronic acid derivatives (Scheme 1). Unfortunately, no desired network polymers (**FPOP-3** and **FPOP-4**) were obtained under the conventional reaction conditions. According to the previous report by Jiang's group,[13] the Suzuki coupling of the similar starting materials without fluorosubstitutent is accomplished smoothly and efficiently under the conventional conditions. In our case, due to effect of multifluoro-substitutents, the efficiency of Suzuki coupling reaction between fluorinated porphyrin monomer **M-1** and diboronic acid derivatives is low under the conventionally used reaction conditions. Therefore, no desired network polymers were obtained.



Scheme 1. Synthesis Attempts for Polymers **FPOP-3** and **FPOP-4**.

In recent years, direct arylation, known as the dehydrohalogenative cross-coupling reactions between unfunctionalized arenes or aromatic compounds and aryl halides, has been interestingly explored for the synthesis of π-conjugated compounds and polymers in order to improve the synthetic efficiency and reduce useless waste.[18,19] Due to the influence of fluorine substituents, the C–H bond of tetrafluorobenzene is acidic and possesses more effective reactivity in the direct arylation.[20,21,22] Our group has investigated efficient preparation of fluorinated porous organic materials[23] through polycondensation between tetrafluorobenzene and aryl halides via C–H direct arylation under the condition reported by Kanbara and Kuwabara.[24,25] The obtained materials exhibit high porosities and the related BET specific surface areas are up to 1000 m^2 g^{-1}.



Scheme 2. Synthesis of **FPOP-5** and **FPOP-6** through Direct C–H Arylation Polymerization.

Considering the chemical structure of **FPOP-3** and **FPOP-4**, we think that direct C–H arylation polycondensation between fluorinated porphyrin monomer **M-2** and corresponding dibromo-substituted aryl rings might be an alternative synthesis method. As a result, monomer **M-2** prepared from 2,3,5,6-tetrafluorobenzaldehyde (Scheme S1, Supporting Information) was coupled with 1,4-dibromobenzene in dimethylacetamide using $Pd(OAc)_2$ (5 mol %) and a phosphine ligand $P(t\text{-}Bu)_2Me\text{-}HBF_4$ (10 mol %) as catalysts in the presence of K_2CO_3 (2 equiv) overnight to afford the desired conjugated fluorinated polyporphyrin **FPOP-3**. Similarly, when 4,4'-dibromo-1,1'-biphenyl was used as linker, **FPOP-4** can also be smoothly obtained. To prove the adaptability of this preparative method, we use 1,2,4,5-tetrafluorobenzene and 4H,4'H-octafluorobiphenyl as linkage monomers to condense with bromo-substituted porphyrin monomer **M-3** giving another kind of fluorinated conjugated polyporphyrins **FPOP-5** and **FPOP-6**, respectively, in this case fluorinated benzene rings are not directly linked with the porphyrin ring.

Compared with commonly used C–C coupling polycondensation, C–H direct arylation exhibits more efficient and advantageous for preparation of fluorinated porous polymers. The C–H bond of tetrafluorobenzene is acidic due to the influence of fluorine substituents and shows more effective reactivity in the direct arylation. Without further transformation to monomers with functional groups such as boric acid or alkyne, the substrates containing tetrafluorobenzene can be directly coupled with aryl halides through C–H direct arylation polycondensation to afford porous polymers.[23]

Because of the cross-linking nature similar to most of reported porous polymers, all the obtained materials can not be soluble in common solvents and exhibit good chemical stabilities. A comparison of the FTIR spectra of all polymers and monomers with wavenumbers from 1800 to 600 cm^{-1} is displayed in Figure S1 (Supporting Information), in which the strong peaks at about 998–1002 cm^{-1} are ascribed to the characteristic N–Fe vibration band.[9] The different species of chemical element in the polymers were also characterized and proven by XPS data (688.3 eV for F 1s, 398.8 eV for N 1s, and 285.3 eV for C 1s) of the materials (Figure 1 and Figure S2, Supporting Information).

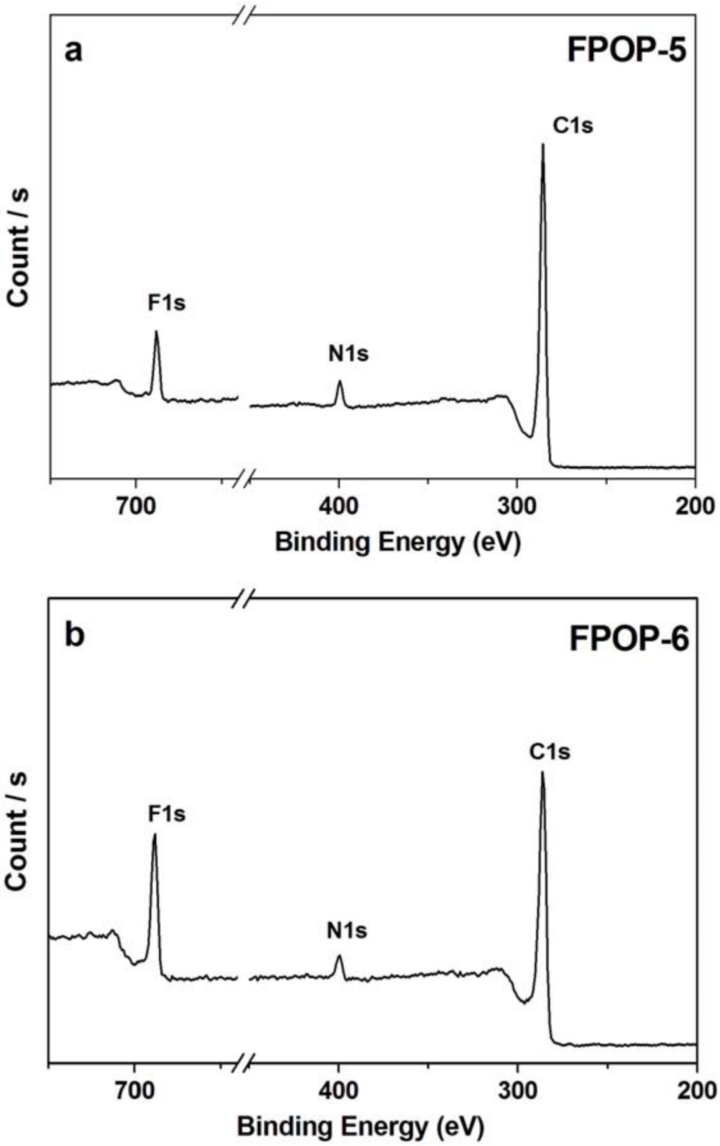


Figure 1. XPS plots of **FPOP-5** (a) and **FPOP-6** (b).

As we known that Fe-porphyrin complex possesses the high-spin paramagnetic effect, ^{13}C CP/MS NMR spectra of all obtained polymers can not give good signal intensities.[13] Therefore, the free-base porphyrin polymers were prepared by the same method for ^{13}C CP/MS NMR spectrum characterization. The signal peak assignments of chemical shifts belonged to porphyrin macrocycle and phenylene moieties (Figure 2 and Figure S3, Supporting Information) are similar to the reported data.[9,13]

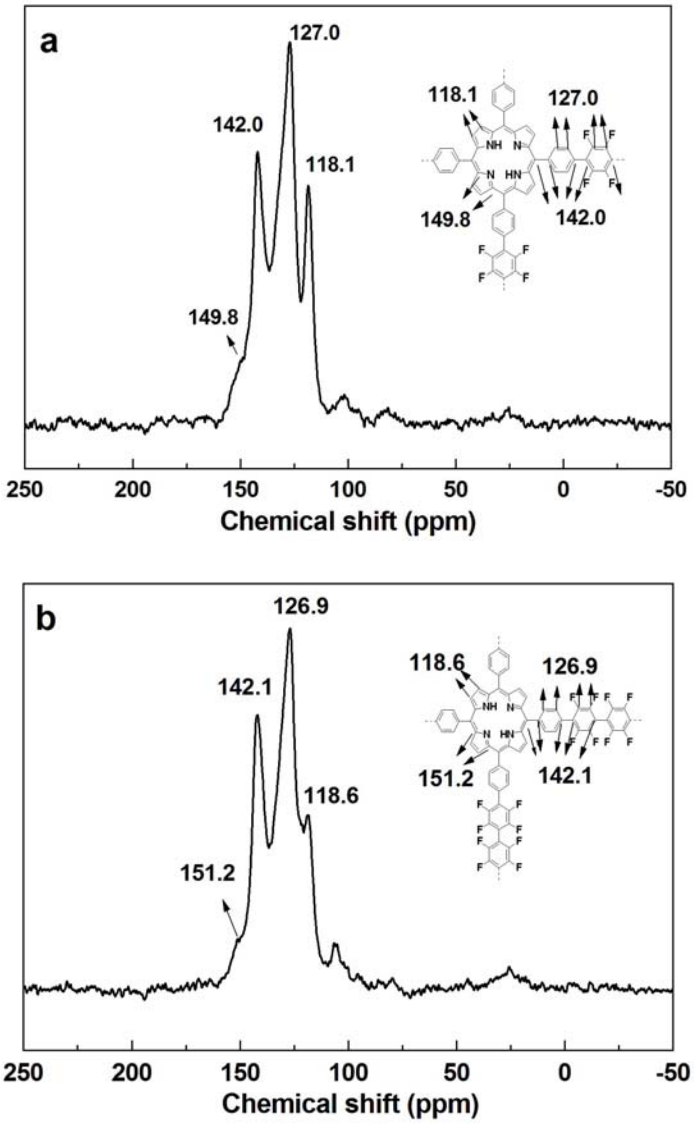


Figure 2. ^{13}C CP/MAS NMR spectra of free-base polyporphyrins related to **FPOP-5** (a) and **FPOP-6** (b).

TGA plots of the polymers and monomers (Figure S4, Supporting Information) indicate the difference of their thermal stabilities. The obtained polymeric networks yield high residual masses of 70~80% (calculation based on the weight of materials after removing adsorbed water at temperature above 100 °C) at a temperature up to

800 °C. For porphyrin monomers, they produce the residual masses of about 50 % at 800 °C. Based on the comparison of different thermogravimetric data belongs to monomers and corresponding polymers, we can infer that preparation of conjugated polyporphyrins through direct C–H arylation polymerization is successful. SEM images (Figure S5, Supporting Information) show that the obtained materials exhibit flake-shaped monoliths or irregular layer-stacked plates.

Nitrogen sorption analysis was examined to investigate the materials' porosities and the corresponding adsorption–desorption isotherms shown in Figure 3a were tested at 77 K. In light of the IUPAC classification,[26] nitrogen sorption isotherms of **FPOP-5** exhibit a combination of type I and II, the other three polymers show a type I nitrogen sorption isotherms. From all the isotherms, we can see apparently the hysteresis within the entire scope of relative pressure because of the adsorbed volume increased linearly during adsorption. The relative pressure (P/P_0) scope from 0.01 to 0.10 was used to calculate the specific surface area value in accordance with the previous reports.[17] The BET specific surface area values of **FPOP-3~6** ranged from 840 to 670 m^2 g^{-1} are at the similar level when compared with the reported porous polymers based on porphyrins prepared through the classic cross coupling methods, for instance, the Suzuki coupling reaction[13] and the Sonogashira–Hagihara coupling reaction.[12] Calculation based on the adsorption branch of isotherms by the NLDFT approach can produce the corresponding PSD profiles (shown in Figure 3b) of the obtained porous materials. We can see that dominant pore sizes of the materials are ranged from 0.50 to 1.31 nm. The data of key porosity of the obtained materials including BET specific surface area, dominant pore size, and pore volume are shown in Table 1. The microporous nature can be found for the materials, which is analogous to most of reported porous organic polymers.

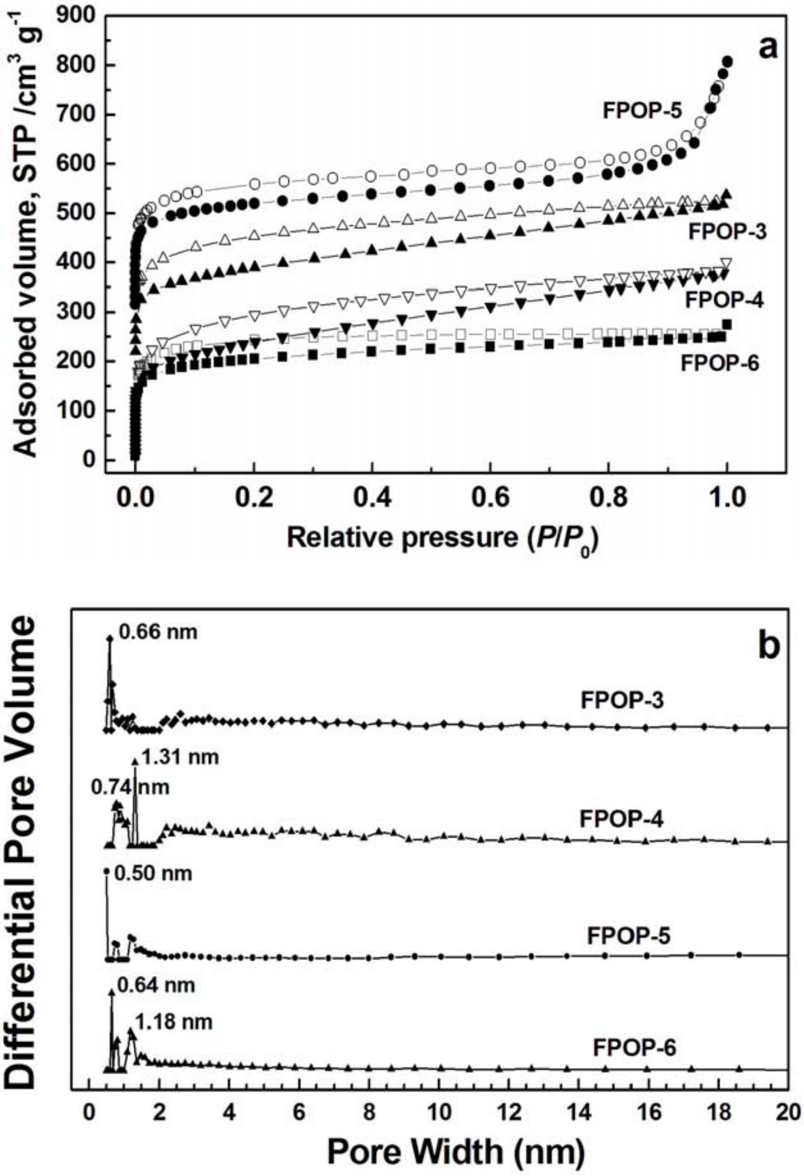


Figure 3. a) Nitrogen adsorption–desorption isotherms of **FPOP-3~6** tested at 77 K, the solid and open symbols are used to mark adsorption and desorption branches, respectively. For clear identification, the isotherms of **FPOP-3** and **FPOP-5** are shifted vertically by 200 and 300 cm^3 g^{-1}, respectively. b) The PSD profiles of **FPOP-3~6** calculated by NLDFT.

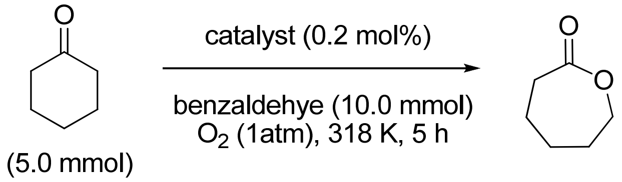
Table 1. Porosity Properties of **FPOP-3~6**.

Polymer	S_{BET} [a] (m^2 g^{-1})	$S_{Langmuir}$ [b] (m^2 g^{-1})	S_{micro} [c] (m^2 g^{-1})	V_{total} [d] (cm^3 g^{-1})	D_{pore} [e] (nm)
FPOP-3	840	1130	290	0.57	0.66
FPOP-4	670	910	195	0.48	0.74,1.31
FPOP-5	760	1010	426	0.75	0.50
FPOP-6	710	940	430	0.39	0.64,1.18

[a] Specific surface area calculated with the BET method. [b] Specific surface area calculated using the Langmuir equation. [c] Micropore surface area calculated according to the t-plot method. [d] Total pore volume at P/P_0=0.99. [e] Data calculated with the NLDFT method. [a,b,c,e] All data are calculated based on the corresponding nitrogen adsorption isotherms.

In organic synthesis, the BV oxidation reaction[27] is usually used for the transformation of ketones to the corresponding esters. As we know, organic peroxy acids often act as oxidants, which are expensive and hazardous. It is not beneficial for environment and cost-effective in the chemical and drug industry. Recently, BV oxidation with molecular oxygen has been reported as a green approach, in which Fe-porphyrin complex is an important homogeneous catalyst accompanied with benzaldehyde. The plausible mechanisms are as follows,[28] dehydrogenation of benzaldehyde with iron(III) porphyrin gives an acyl radical, which is treated with dioxygen and benzaldehyde to generate peroxybenzoic acid, then another iron porphyrin molecule is oxidized by the peroxybenzoic acid to afford high-valent Fe porphyrin intermediate PorFeV=O, which can react with ketone through the oxygen transfer step to generate the desired lactone. We can see that the roles of Fe-porphyrin porous polymer are an initiator to promote the acyl radical production and an oxygen atom carrier as intermediate PorFeV=O.

Table 2. The Aerobic Oxidation of Cyclohexanone Catalyzed by **FPOP-3~6**.



Entry	Catalyst	Selectivity (%)	Yield (%)				
			1st run	2nd run	3rd run	4th run	5th run
1	**none**	>99	15	–	–	–	–
2	**M-2**	>99	99	–	–	–	–
3	**FPOP-3**	>99	98	95	91	89	85
4	**FPOP-4**	>99	92	90	86	85	81
5	**FPOP-5**	>99	89	84	80	72	66
6	**FPOP-6**	>99	85	81	75	70	63

In order to test the catalytic activities of the obtained polymers as heterogeneous catalyst, BV oxidative transformation of cyclohexanone to *ε*-caprolactone using molecular oxygen as oxidant was used for a model reaction shown on Table 2. The control reaction indicates the low transformation in the absence of catalyst, implying that the obtained porous polymer can perform as the efficient catalyst in the reaction. When monomer **M-2** is used as a homogeneous catalyst, its catalytic performance is more efficient without considering the recycling and separation problems. However, as to the homogeneous catalytic processes in industrial manufacture, some drawbacks such as high cost, recovering problems, and pollutions caused by heavy metal are unavoidable. We believe that the heterogeneous catalytic systems can resolve these problems, because they are recyclable and reusable catalyst systems.[29] Especially, the porous materials as catalyst are beneficial to the heterogeneous catalysis process, since the short channels of the porous materials are favorable for mass transfer.[30,31,32]

Porous polyporphyrins **FPOP-3~6** are used as heterogeneous catalysts, although their catalytic activities might be not higher than the homogeneous catalyst. Under the given reaction conditions, the yields for *ε*-caprolactone (near up to 100% selectivity) are ranged from 98% to 85% based on different porous conjugated polyporphyrins. The porous structure derived from Fe-porphyrin network is beneficial for the reactant molecules accessible to contact with the catalytic sites through the channels and accelerating the molecular diffusion of reactants and products, which lead to the comparable catalytic effect with the Fe-porphyrin complex molecule as homogeneous catalyst (Entry 2 in Table 2). Meanwhile, we can see that the catalytic activities of fluorinated conjugated polyporphyrins containing the fluorinated phenyl substituents (**FPOP-3** and **FPOP-4**, Entries 3 and 4, Table 2) are higher than those of **FPOP-5** and **FPOP-6** (Entries 5 and 6, Table 2).

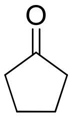
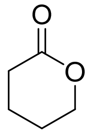
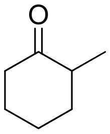
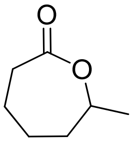
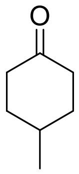
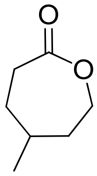
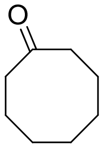
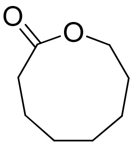
All prepared porous catalysts are easily recycled using a simple centrifugation process and subsequent drying in vacuum overnight before being reused. For the fifth catalytic cycle promoted by porous conjugated polyporphyrins **FPOP-3** and **FPOP-4** under the given reaction conditions, the yields for *ε*-caprolactone are still up to 80%. For comparison, the catalytic reactions by **FPOP-5** and **FPOP-6** were also done; but the corresponding yields have decreased to about 65% (Entries 5 and 6, Table 2). **FPOP-3** with high porosity exhibits the best catalytic efficiency and recycling effect.

According to the reasonable mechanisms, high-valent Fe porphyrin intermediate PorFeV=O is key intermediate in the catalytic transformation in the main step. However, as the side step, it can also promote the oxidative breakdown of the porphyrin ligand,[6] which leads to the decrease of the amount of effective porphyrin as catalyst sites in every recycling. Therefore, the yield of the catalytic reaction is gradually decreasing when using the recycled catalyst every times.

As mentioned above, the fluorinated phenyl substituents of the Fe-porphyrin (**FPOP-3** and **FPOP-4**) are beneficial to the conversion, due to their stabilization of porphyrin to restrain the catalyst breakdown. As to **FPOP-5** and **FPOP-6**, the fluorinated benzene rings are just linkers between tetrakis(2,3,5,6-phenyl) porphyrin units and have less positive effects on the porphyrin stability. This is the main reason why the catalytic activities of **FPOP-3** and **FPOP-4** are higher than those of **FPOP-5** and **FPOP-6**, even the porosity of **FPOP-5** is a little bit higher than that of **FPOP-4**. However, as for **FPOP-3** and **FPOP-4** with similar structure, the catalytic activity of **FPOP-3** is higher than that of **FPOP-4**, which might be ascribed to the higher specific surface area and pore volume of **FPOP-3**.

The BV oxidative transformation of different cycloketones promoted with the **FPOP-3** was studied under the oxygen atmosphere and mild conditions (Table 3). Among all of the cycloketones, six-membered cycloketones with or without methyl substitutes are most efficiently transformed into the corresponding lactones, considering that proper steric configuration of the cycloketones is favorable to the large ring of the metalloporphyrin molecular stucture.[29] The six-membered cycloketone was more easily oxidized, when compared with cyclopentanone and cyclooctanone in the same conditions. Except cyclooctanone, most cycloketones can be transformed into corresponding lactones with satisfied yields (Entries 1–3, Table 3). Due to bulky molecular structure, only 6 % yield of lactone in the oxidation of cyclooctanone (Entry 4, Table 3) was obtained, which was consistent with the metalloporphyrins-catalyzed system.[33]

Table 3. BV Oxidation of Ketones Using **FPOP-3** as Catalyst [a]

Entry	Substrate	Product	Selectivity (%)	Conversion (%)	Yield (%)
1			>99	86	86
2			>99	91	91
3			>99	97	97
4			>99	6	6

[a] Ketone (5.0 mmol), benzaldehyde (10.0 mmol), DCE (15 mL), **FPOP-3** (0.2 mol%) , O_2, 5 h, 45 °C.

Conclusions

In summary, Fe-porphyrin has been widely used as biomimetic catalyst for oxidative transformation in synthetic chemistry. Formation of Fe-porphyrin-incorporating porous polymers can stabilize Fe-porphyrin catalysts in oxidation chemistry. Owing to the influence of fluorine substituents, the C–H bond of tetrafluorobenzene is acidic and possesses more effective reactivity in the direct arylation, fluorinated Fe-porphyrin conjugated porous polymers (**FPOP-3~6**) were prepared through direct C–H arylation polymerization. The obtained materials are chemically and thermally stable, exhibit permanent porous nature with high BET specific surface area up to 840 m^2 g^{-1}. Considering highly catalytic activity of fluorinated Fe-porphyrin, BV oxidation of cycloketones to corresponding lactone with molecular oxygen was used to test catalytic activities of the obtained polymers as heterogeneous catalyst. The fluorinated phenyl substituents of the Fe-porphyrin are not only beneficial to the conversion, but also can stabilize porphyrin to restrain the catalyst decomposition. Meanwhile, the Fe-porphyrin porous structure is helpful for reactant molecules accessible to contact with the catalytic site through the different pores and accelerating the molecular diffusion of reactants and products, which lead to the good catalytic efficiency.

Experimental Section

Materials. 1,4-Dibromobenzene, 4,4'-dibromo-1,1'-biphenyl, and palladium acetate were commercially available from Acros company. Di-*tert*-butyl(methyl)phosphonium tetrafluoroborate, 4H,4'H-Octafluorobiphenyl , and 1,2,4,5-tetrafluorobenzene were commercially available from Sigma-Aldrich company. Benzene-1,4-diboronic acid and biphenyl-4,4'-diboronic acid were commercially available from J&K chemical company. Various cyclic ketones and benzaldehyde were commercially available from Aladdin chemical company. 2,3,5,6-Tetrafluorobenzaldehyde,[34] iron(III) 5,10,15,20-Tetrakis (2,3,5,6-tetrafluoro-4-iodophenyl)porphyrin (**M-1**),[35] and iron(III) 5,10,15,20-Tetrakis(4-bromophenyl)porphyrin (**M-3**)[13] were obtained according to the reported synthetic methods. The other chemical reagents and solvents were commercially available for direct use.

Instrumental Characterization and Structural Analysis. The detail information was shown in the Supporting Information.

Synthesis of Iron 5,10,15,20-Tetrakis(2,3,5,6-tetrafluorophenyl) Porphyrin (M-2). To a round-bottom flask (250 mL) with 2,3,5,6-Tetrafluorobenzaldehyde (0.354 g, 1.16 mmol) and pyrrole (0.081 mL, 1.16 mmol) in dichloromethane (125 mL)was added $BF_3 \cdot Et_2O$ (0.5 mL, 3.95 mmol) dropwise under argon at room temperature. The resulting solution was stirred for 1 h, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.55 g) and pyridine (1.6 mL) were added subsequently After being stirred overnight, the final mixture was filtered through a short column (silica gel) and washed with dichloromethane. Evaporation of the solvent under reduced pressure gave a brown solid residue, which was further purified by flash silica gel column chromatography using chloroform as eluent. The first fraction was collected and evaporated to afford 5,10,15,20-tetrakis(2,3,5,6-tetrafluorophenyl) porphyrin ([p-H, $4F]_4P$) as a purple red solid (0.070 g, 10%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 8H), 7.68–7.60 (m, 4H),

–2.87 (s, 2H). ^{19}F NMR (375 MHz, $CDCl_3$): δ –137.24 (m, 8F), –138.57 (m, 8F). UV–vis (λ_{max}, nm, $CHCl_3$): 413, 507, 583. MS (MALDI-TOF): m/z calculated for $C_{44}H_{14}F_{16}N_4$: 902.60 [M]; found: 902.20 [M].

To the obtained porphyrin (0.65 g, 0.72 mmol) in DMF (150 mL) was added $FeCl_2 \cdot 4H_2O$ (3.56 g, 18 mmol). The resulting mixture was heated to 140 °C and stirred overnight. The reaction solution was cooled to room temperature and an aqueous hydrochloric acid was added dropwise. The precipitate was formed and collected by filtration. After being washed with aqueous hydrocholoric acid solution (3.0 M, 20 mL) and H_2O (200 mL×2), **M-2** was obtained as purple black powder and dried in a vacuum condition (0.69 g, 97%). UV–vis (λ_{max}, nm, $CHCl_3$): 268, 351, 412, 503, 629. IR: υ (cm^{-1}): 2926 (w), 1646 (w), 1499 (s), 1393 (m), 1328 (m), 1268 (m), 1174 (m), 1002 (m), 954 (s), 940 (s), 852 (m), 777 (m), 709 (s). MS (MALDI-TOF): m/z calculated for $C_{44}H_{14}F_{16}N_4FeCl$: 992.10 [M]; found: 991.70 [M].

Synthesis of FPOP-3. A 10 mL Schlenk tube was charged with **M-2** (153 mg, 0.15 mmol), 1,4-dibromobenzene (75 mg, 0.3 mmol), $Pd(OAc)_2$ (10.0 mg, 0.04 mmol), K_2CO_3 (50 mg, 0.3 mmol), $P(t\text{-}Bu)_2Me\text{-}HBF_4$ (20 mg, 0.08 mmol). Dimethylacetamide (DMAc, 2.5 mL) was added dropwise to the mixture and the resulting suspension was stirred for 0.5 h at room temperature under a nitrogen atmosphere. When degassed by three freeze–pump–thaw cycles, the resulting suspension was stirred at 130 °C overnight under the nitrogen atmosphere. The dark violet solid was formed and filtered. After being washed with methanol (50 mL×3) and THF (50 mL×3), that the obtained solid was extracted with methanol for 24 h in a

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Soxhlet extractor, and then with tetrahydrofuran for another 24 h to give a black solid followed by drying in vacuum (220 mg, 96%).

Synthesis of FPOP-4. A 10 mL Schlenk tube was charged with **M-2** (153 mg, 0.15 mmol), 4,4'-dibromo-1,1'-biphenyl (93.1 mg, 0.3 mmol), $Pd(OAc)_2$ (10.0 mg, 0.04 mmol), K_2CO_3 (50 mg, 0.3 mmol), $P(t\text{-}Bu)_2Me\text{-}HBF_4$ (20 mg, 0.08 mmol), and DMAc (2.5 mL). The mixture was passed through the same synthetic procedure as **FPOP-3** to furnish **FPOP-4** as a black solid (230 mg, 93%).

Synthesis of FPOP-5. A 10 mL Schlenk tube was charged with **M-3** (215 mg, 0.20 mmol), 1,2,4,5-tetrafluoro-benzene (60 mg, 0.4 mmol), $Pd(OAc)_2$ (10.0 mg, 0.02 mmol), K_2CO_3 (83 mg, 0.3 mmol), $P(t\text{-}Bu)_2Me\text{-}HBF_4$ (20 mg, 0.04 mmol), and DMAc (2.5 mL). The mixture was passed through the same synthetic procedure as **FPOP-3** to give **FPOP-5** as a dark solid (220 mg) in the isolation yield of 80%.

Synthesis of FPOP-6. A 10 mL Schlenk tube was charged with **M-3** (215 mg, 0.20 mmol), 4H,4'H-octafluoro-biphenyl (120 mg, 0.4 mmol), $Pd(OAc)_2$ (10.0 mg, 0.02 mmol), K_2CO_3 (83 mg, 0.3 mmol), $P(t\text{-}Bu)_2Me\text{-}HBF_4$ (20 mg, 0.04 mmol), and DMAc (2.5 mL). The mixture was passed through the same synthetic procedure as **FPOP-3** to afford **FPOP-6** as a dark solid (284 mg) in the isolation yield of 85%.

Study on the BV Oxidative Transformation of Ketones Catalyzed by FPOPs. In a typical reaction procedure, to a suspension of catalyst (0.2 mol %) in 15 mL of l,2-dichloroethane were added to ketone (5.0 mmol) and benzaldehyde (10.0 mmol). The resulting mixture was stirred at 45 °C, and then dioxygen was bubbled into the reaction solution. For recycling studies, the polymeric catalyst was firstly recovered by centrifugation and washed with 1,2-dichloroethane for several times. After being dried in vacuum overnight, the catalyst can be reused in a next catalytic run. The consumption of ketones and production of esters can be monitored by gas chromatography. The product yields were calculated with the consumed amount of ketones in the reactions. The conversion of ketones, selectivity, and yield of lactones were studied and calculated by the following equations, Conversion = (moles of converted ketone/moles of initial ketone) × 100%; Selectivity = (moles of formed lactone/moles of converted ketone) × 100%; Yield = (moles of formed lactone/moles of initial ketone) × 100%.

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Supporting Information. Instrumental characterization and structural analysis; synthetic scheme to **M-2**; IR spectra of spectra of all polymers and monomers; XPS plots and ^{13}C CP/MAS NMR spectra of **FPOP-3** and **FPOP-4**; TGA curves of the polymers and monomers under nitrogen atmosphere; SEM images of all the polymers; Ultra–violet and visible spectra, ^{1}H NMR, ^{13}C NMR, and MS of new compounds.

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