

## Supporting information

### Synthesis of TEMPO Radical Decorated Hollow Porous Aromatic Frameworks for Selective Oxidation of Alcohols

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### Table of contents

<b>1. General Methods and Materials</b>	<b>S2</b>
<b>2. Experimental Sections</b>	<b>S3</b>
<b>3. Characterization of hollow and non-hollow PAFs-TEMPO</b>	<b>S6</b>
<b>4. References</b>	<b>S13</b>

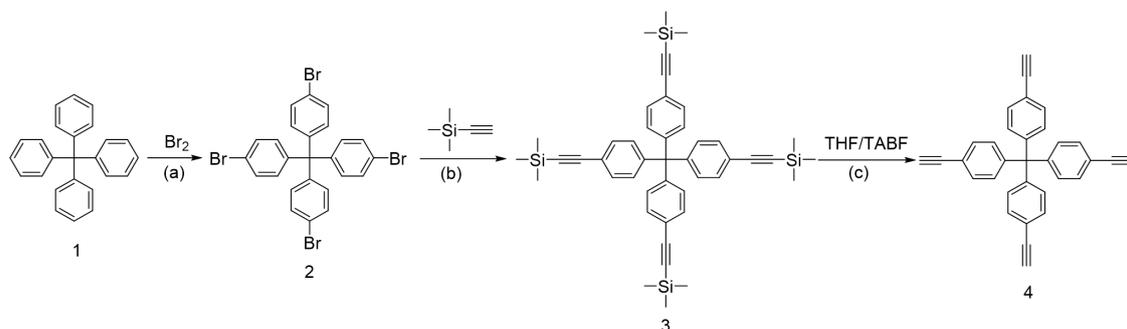
## 1. General Methods and Materials

All the chemicals were obtained from commercial sources, unless otherwise noted, and used without further purification (Innochem, J&K, TCI, and Aladdin). All of the reactions and manipulations were carried out under nitrogen with the use of standard inert atmosphere and Schlenk technique unless otherwise indicated. Column chromatography was performed with 200-300 mesh neutral silica gels. The sorption isotherm measurements were performed on an ASAP (Accelerated Surface Area and Porosimetry) 2020 System. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The pore volume and pore size distribution were derived from the sorption curve by using the non-local density functional theory (NLDFT) model. Before gas adsorption measurement, sample was dried again using the “outgas” function of the surface area analyzer for 5 h at 313 K. Powder X-ray diffractions (PXRD) were recorded on a Rigaku Ultima IV diffractometer using Cu K  $\alpha$  1 (1.5418 Å) radiation, from 3-50°. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449F3 in a nitrogen or oxygen atmosphere at a heating rate of 5 °/min. EPR spectra were measured by Bruker EMX-10/12 spectrometer at ambient temperature. SEM images were recorded using Hitachi S-4800. TEM images were obtained with a JEM-2100 microscope operated at 200 kV. FT-IR spectra were collected with a NICOLET 6700 Fourier Transform Infrared Spectrometer at a resolution 4 cm<sup>-1</sup>. GC analysis was measured on GC-9160. General GC conditions for: Restek column, 30 m x 0.32 mm x 0.5 mm; FID detector; carrier gas: N<sub>2</sub>; area normalization. Column Conditions for a benzyl alcohol, 5-HMF, 4-methoxybenzyl alcohol, 4-tert-butylbenzyl alcohol, 4-fluorobenzyl alcohol, 4-nitrobenzyl alcohol,  $\alpha$ -methylbenzyl alcohol, benzhydrol, 2-thiophenemethanol, furfury alcohol, 1-indanol, 3-pyridinemethanol, and their corresponding carbonyl compounds: column temperature: 80 °C for 5 min, rising to 250 °C at a rate of 20 °C/min.

## 2. Experimental sections

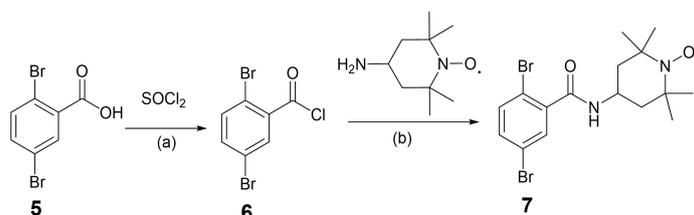
### 2.1 Synthesis of tetrakis(4-ethynylphenyl) methane and 2, 5-dibromo-(2,2,6, 6-tetramethylpiperidine) benzamide

tetrakis(4-ethynylphenyl) methane (2) was synthesized according to previous report with modification<sup>[1]</sup>



Scheme S1. Reaction conditions: (a) Br<sub>2</sub>, stirring at room temperature for 20 minutes; (b) PPh<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, diisopropylamine, 24 h reflux; (c) TBAF, THF, stirring at room temperature for 2 h.

2, 5-dibromo-(2,2,6, 6-tetramethylpiperidine) benzamide, was based on our previous report<sup>[2]</sup>:



Scheme S2. Reaction conditions: (a) SOCl<sub>2</sub>, 80 °C, 1.5 hours; (b) dry DCM, triethylamine, 4-NH<sub>2</sub>-TEMPO, room temperature, 24 hours.

### 2.2 Synthesis of HPAF-TEMPO

Silica nanospheres (500 mg g, 215 nm), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (8.4 mg) and CuI (2.3 mg) were added in a round bottle under N<sub>2</sub>, followed by the addition of toluene (15 mL) and triethylamine (15 mL). The mixture was sonicated for 15 min under N<sub>2</sub>. Tetrakis(4-ethynylphenyl)methane (50 mg, 0.12 mmol) and

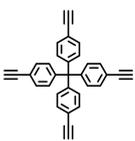
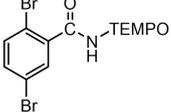
2,5-dibromo-(2,2,6,6-tetramethylpiperidine)benzamide (103 mg, 0.24mmol) were added to the mixture under N<sub>2</sub>. The mixture was heat slowly from room temperature to 100 °C in an oil bath, and kept in this temperature for 48 h with gentle stirring. The mixture was cooled down to room temperature, and the yellowish precipitate was isolated by centrifugation. After being successively washed with excess CH<sub>3</sub>Cl, acetone, and methanol, the obtained SiO<sub>2</sub>@PAF-TEMPO were dried under vacuum at 60 °C. The removal of SiO<sub>2</sub> was done by adding the SiO<sub>2</sub>@PAF-TEMPO (0.30 g) into a HF solution (20 mL, 10% aqueous solution) and stirred for 2 h. The resultant hollow PAF-TEMPO were collected by centrifugation, washed successively with water and ethanol, and dried at oven under 60 °C. For the preparation of non-hollow PAF-TEMPO, the same procedure was used but without the use of SiO<sub>2</sub> nanospheres.

### **2.3 Catalysis studies of HPAF-TEMPO**

Typical procedure for aerobic oxidation of alcohols. To a 10 mL screw capped vial was added 5-HMF (0.28 mmol), catalysts (10 mg, 0.014 mmol of TEMPO based on the calculation of element analysis, 5 mol%), benzotrifluoride (PhCF<sub>3</sub>, 0.5 mL, saturated with O<sub>2</sub>), and TBN (0.05 mmol), the vial was sealed and placed in oven (80 °C) for desired time. After cooling to room temperature, 0.5 mL DCM and p-nitrobenzene (internal standard, 0.28 mmol) were added and the catalysts were removed by centrifugation. The clear solution was dried with Na<sub>2</sub>SO<sub>4</sub>, and analyzed by GC without further purification. For cycling experiments, the catalysts were collected by centrifugation, washed with ethanol twice and dried in oven.

### 3. Characterizations of hollow and non-hollow PAFs-TEMPO

Table S1. Various conditions for the synthesis of HPAF-TEMPO.

	SiO <sub>2</sub>			Temp.	TEA mL	Toluene mL
S1	500 mg	0.12 mmol 50 mg	0.24mmol 103 mg	100 °C	15	15
S2	<b>300 mg</b>	0.12 mmol 50 mg	0.24mmol 103 mg	100 °C	15	15
S3	<b>50 mg</b>	0.12 mmol 50 mg	0.24mmol 103 mg	100 °C	15	15
S4	500 mg	0.12 mmol 50 mg	0.24mmol 103 mg	100 °C	<b>20</b>	<b>20</b>
S5	500 mg	0.12 mmol 50 mg	<b>0.12mmol 52mg</b>	<b>70°C</b>	15	15
S6	500 mg	0.12 mmol 50 mg	0.24mmol 103 mg	100 °C	<b>3</b>	15

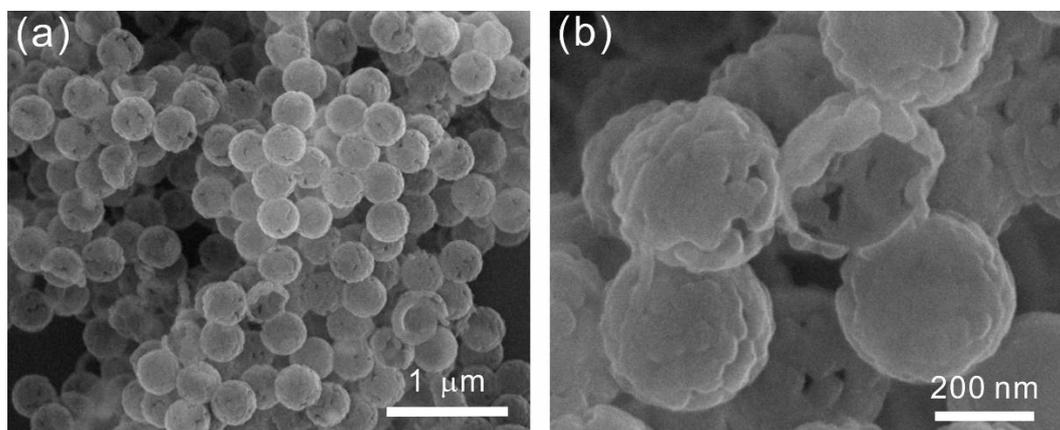


Figure S1. SEM images of HPAF-TEMPO.

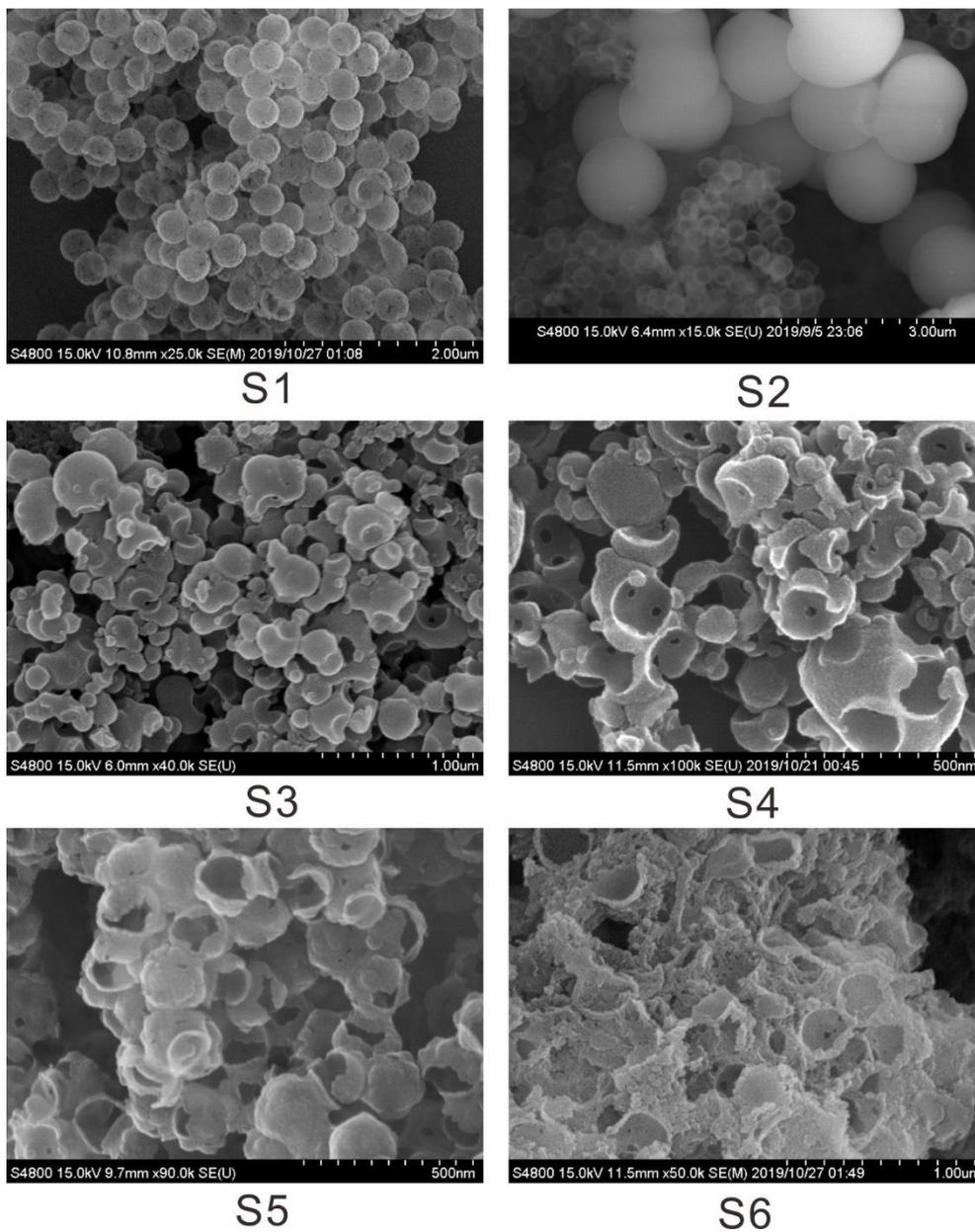


Figure S2. SEM images of HPAF-TEMPO synthesis by using the conditions listed in Table S1.

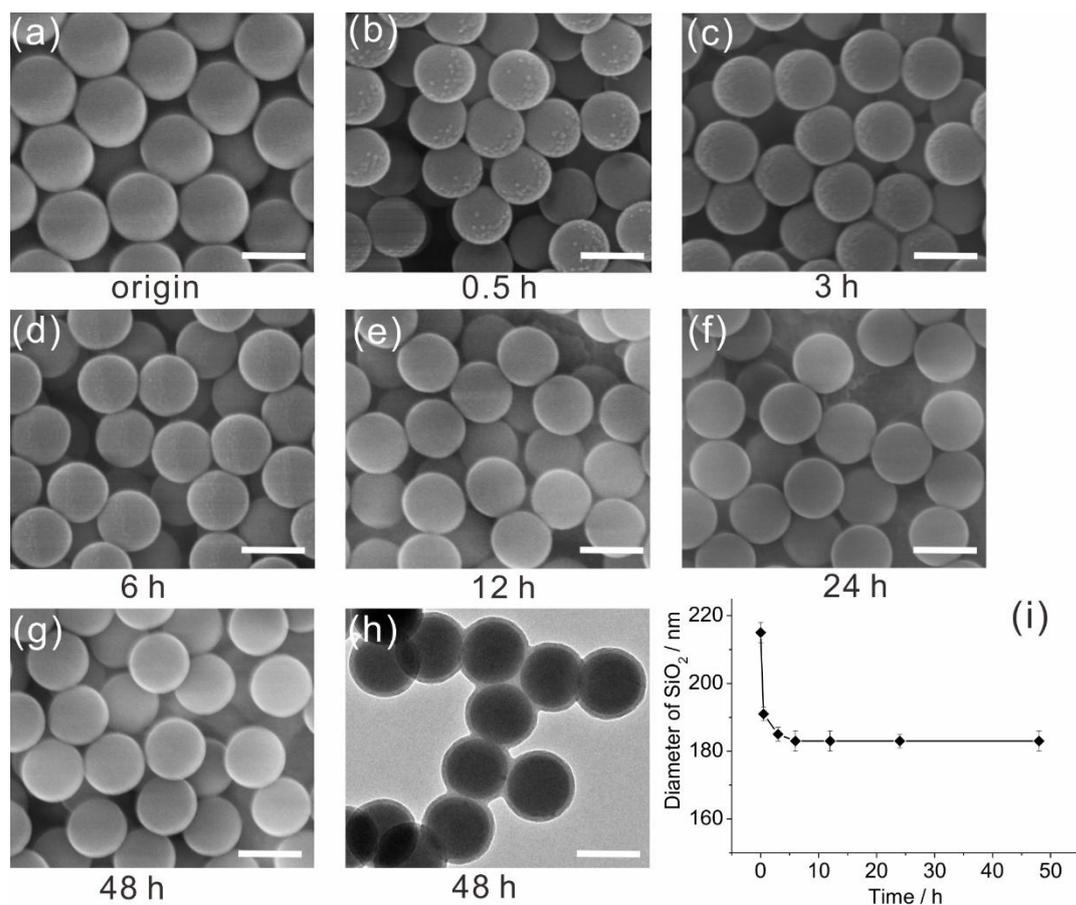


Figure S3. SEM images of original SiO<sub>2</sub> nanoparticles and treated in the mixture of toluene and triethylamine at 100 °C for varied time. The size of SiO<sub>2</sub> nanospheres dramatically decreases to 191 nm within 30 min, then slowly decreases to 183 nm after 3 h, and this size does not change during the rest of reaction time. These results indicate that despite the slightly etching effect of SiO<sub>2</sub> nanospheres in basic solvents, they are stable enough to serve as templates for the growth of PAF-TEMPO shells. Scale bar = 200 nm.

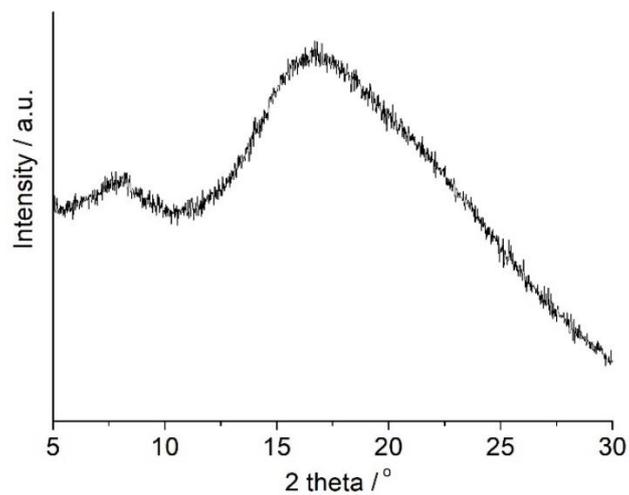


Figure S4. Power X-ray pattern of the HPAF-TEMPO.

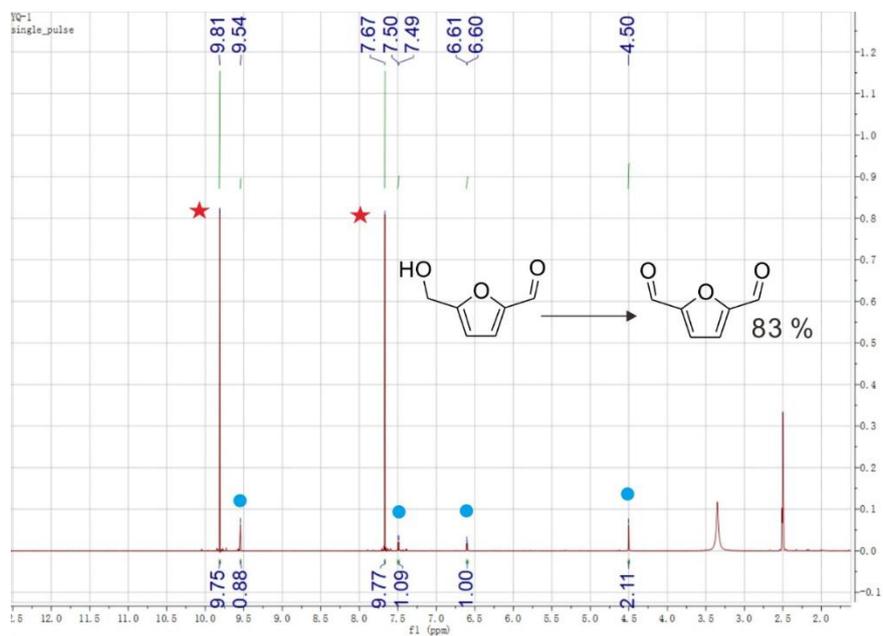


Figure S5. <sup>1</sup>H NMR spectrum of the oxidation of 5-HMF by HPAF-TEMPO after 4 h.

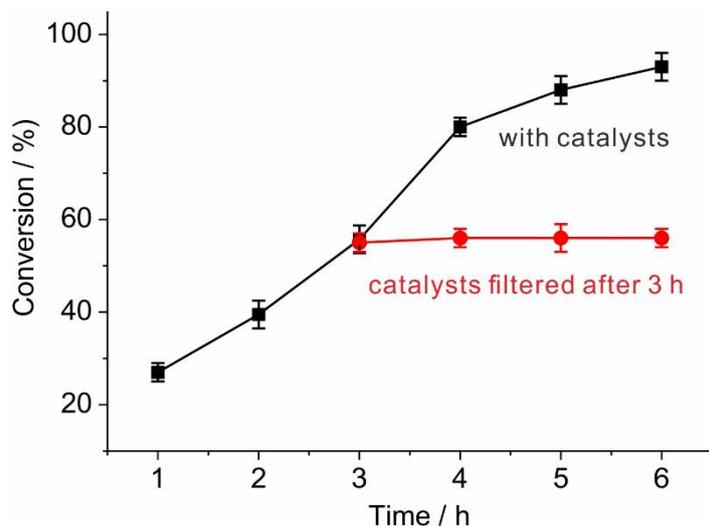


Figure S6. Plots of GC conversion (%) versus time for the oxidation of 5-HMF catalyzed by HPAF-TEMPO. (red squares) and non-hollow PAF-TEMPO microspheres (black dots),

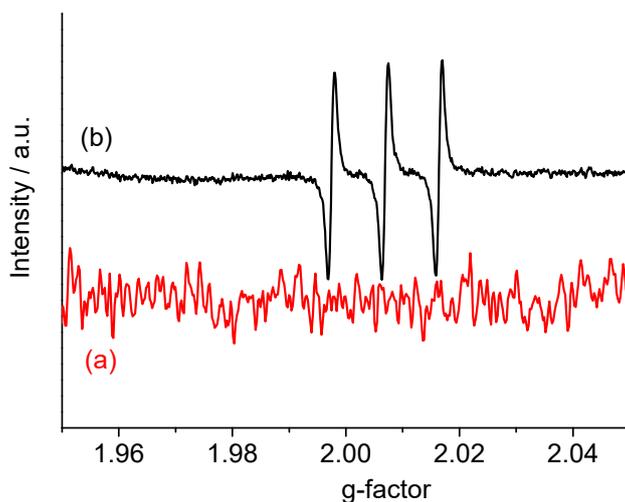


Figure S7. EPR spectra of (a) filtrated solution after catalysis and (b) monomer **2** solution with concentration of 0.5 mM. Assuming the catalytic reaction leads to 10% of TEMPO leached from the solid catalyst to the solution. Simple calculation suggests that there is 2.8 mM of free TEMPO radicals in the solution ( $0.014 \text{ mmol} \times 10\% / 0.5 \text{ mL} = 2.8 \text{ mM}$ ), which should be detectable by the EPR spectra, since the 0,5 mM of monomer **2** shows clear triple-peak pattern. However, no peak was observed in the EPR spectrum of the filtrated solution, indicating that the no detectable free TEMPO leached from the HPAF-TEMPO after catalysis.

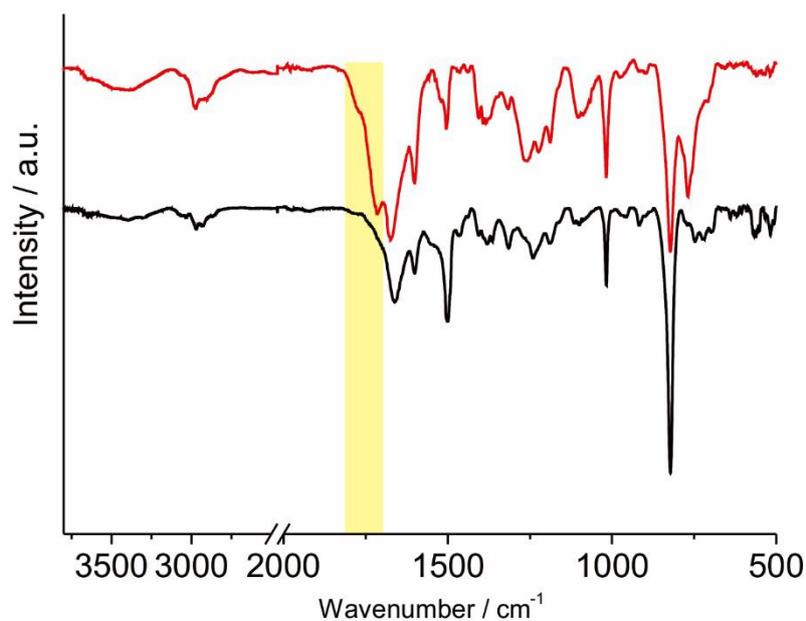


Figure S8. FT-IR spectra of the original HPAF-TEMPO (black) and the one after used for 3 cycles (red). In order to see the increased C=O group, the benzyl alcohol was used as substrates for the recycling experiments. The increased intensity of C=O (1785-1850 cm<sup>-1</sup>, yellow strip) after catalysis hints the partial blockage of HPAF-TEMPO by benzaldehyde.

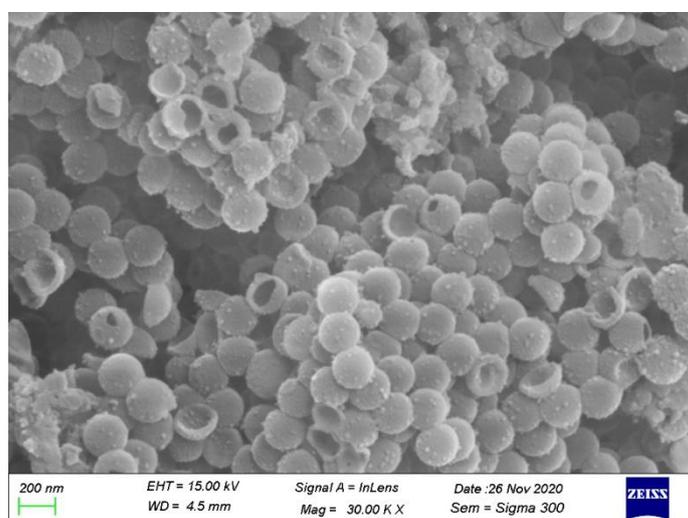


Figure S9. SEM image of the HPAF-TEMPO used for 3 cycles.

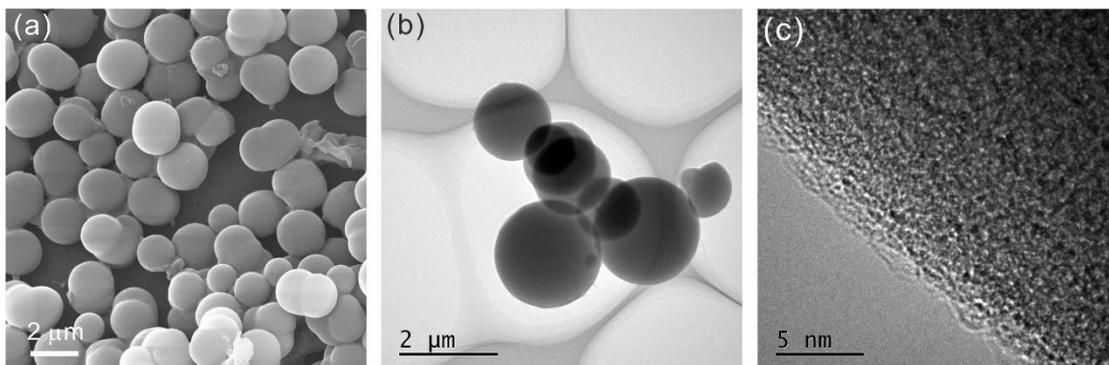


Figure S 10. (a) SEM image and (b, c) TEM images of non-hollow PAF-TEMPO microspheres

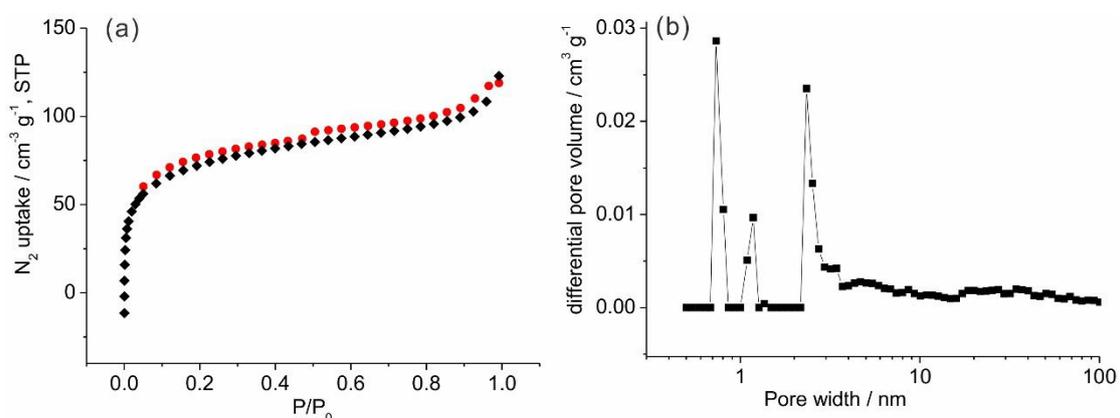


Figure S11. (a)  $N_2$  adsorption/desorption isotherms (Black: adsorption, Red: Desorption), and (b) NLDFT pore size distribution of non-hollow PAF-TEMPO microspheres.

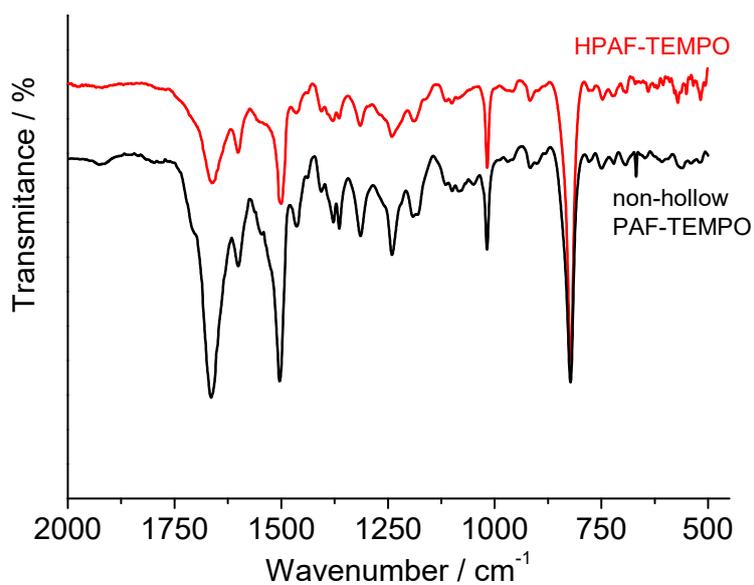


Figure S12. FT-IR spectra of hollow and non-hollow PAFs-TEMPO.

Table S2. Summary of TEMPO-based heterogeneous catalysts for the oxidation of alcohols.

Catalyst	Sub.	Sol.	mol %	Temp. °C	T h	Br-cont ain	Con. (%)	Ref.
HPAF-TEMPO	benzhydrol	PhCF <sub>3</sub>	5	80	9	-	>99	This work
UiO-66-14%	benzhydrol	DCE	1	80	24	-	71	Ref3
UiO-67-38%	benzhydrol	DCE	1	80	24	-	74	Ref3
UiO-67-100%	benzhydrol	DCE	1	80	24	-	>99	Ref3
UiO-68-TEMPO	benzhydrol	DCE +H <sub>2</sub> O	5	80	24	-	88	Ref2
UiO-67-bpy-Eu &TEMPO	benzhydrol	PhCH <sub>3</sub> +HOAc	2	60	18	-	49	Ref4
SBA-15	benzhydrol	HOAc	1	50	6	Bu <sub>4</sub> NBr	0	Ref5
iGO-TEMPO	benzhydrol	DCM+ HOAc	1	25	20	-	9	Ref6
GO-TEMPO	benzhydrol	DCM+ HOAc	1	25	20	-	25	Ref6
TEMPO-CMP-4	2-hexanol	HOAc	5	25	6	-	64	Ref7
TEMPO-CMP-4	2-hexanol	HOAc	5	25	6	DBDMH	95	Ref7
FRPCP	2-hexanol	C <sub>2</sub> D <sub>2</sub> Cl <sub>4</sub>	3.5	80	96	-	94	Ref8

Bu<sub>4</sub>NBr: tetrabutylammonium bromide; DBDMH: 1,3,-dibromo-5,5-dimethylhydantoin

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