Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Nitroxyl Radical Based Conjugated Microporous Polymers as Heterogeneous Catalysts for Selective Aerobic Alcohol Oxidation

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Contents

Section 1. Materials and Methods

1,3-dibromo-5-methylbenzene, carbazole, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-Hydroxy-TEMPO) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) were purchased from commercial sources. All chemicals were of analytical grade and were used without further purification except chloroform was dried by sodium.

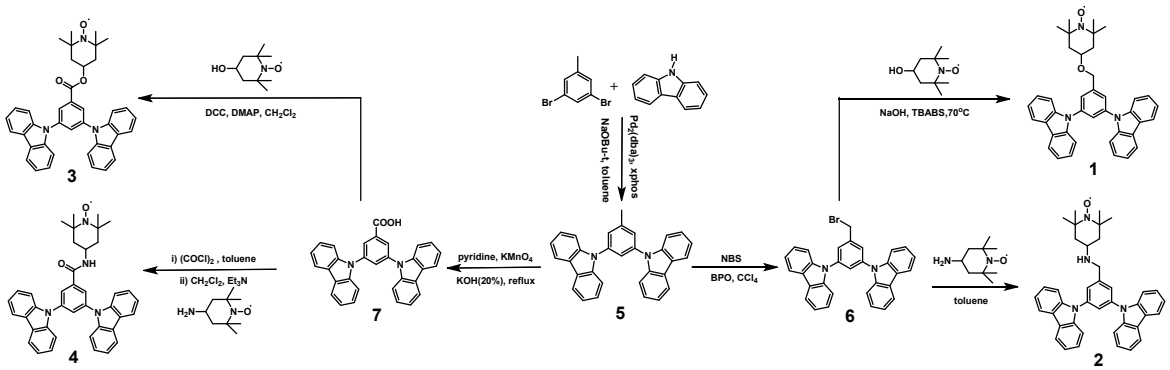
Fourier transform infrared (FT-IR) spectra were recorded in transmission mode on a Bruker Alpha spectrometer using KBr pellets within the range 400–4000 cm^{-1}. ^{13}C cross-polarization magic angle spinning (CP/MAS) spectra were recorded with a 4 mm double resonance MAS probe and at a MAS rate of 10.0 kHz with a contact time of 2 ms (ramp 100) and a pulse delay of 3 s. Thermal gravimetric analysis (TGA) was carried out on a differential thermal analysis instrument (TA Instruments TGA Q50-1918 analyzer) over the temperature range from 20 to 800 °C under N_2 atmosphere with a heating rate of 10 °C min^{-1} using an empty Al_2O_3 crucible as the reference. The surface area were measured by nitrogen adsorption and desorption at 77 K using a BELSORP-mini II analyzer and the samples were degassed at 120 °C for 4 h under vacuum (10^{-5} bar) before analysis. Pore size distribution was calculated from the adsorption branch with the nonlocal density functional theory (NLDFT). Powder X-ray diffraction (PXRD) was performed on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. Electron-Paramagnetic Resonance (EPR) spectra were recorded in solid state using a Bruker-BioSpin spectrometer with a frequency counter from 1 GHz to 10 GHz. The g-factor corrections were obtained using the DPPH (g = 2.0037) as a standard. High resolution imaging of the polymer morphologies was obtained using a Hitachi S-4800 cold field emission scanning electron microscope (FE-SEM). HRTEM was carried out on a JEOL JEM-2100F electron microscope with a LaB_6 filament operated at 200 kV. Elemental analysis (C, H, N) was analyzed on a Perkin-Elmer 240C elemental analyzer. The residual Fe content was determined by inductively coupled plasma mass spectrometry (ICP-MS) using Agilent 7700X ICP-MS model. The samples were prepared by nitrohydrochloric acid digestion before measurement.

***Oxidation of Primary and Secondary Benzylic Alcohols*:** Typical reaction conditions for the oxidation of alcohols were as follows: TEMPO-CMP (12 mg, 5 mol% nitroxide radicals), $NaNO_2$ (4.2 mg, 20 mol%), and DBDMH (4.3

mg, 5 mol%) were placed in a 10 mL glass reaction tube, and CH_3COOH (0.4 ml) and corresponding alcohol (0.3 mmol) were added and stirred at room temperature with an oxygen balloon. After the reaction was completed, the catalyst was separated from the system by filtration and the filtrate was diluted with methanol, then neutralized by $NaHCO_3$ and dried over $MgSO_4$. The products were analyzed by gas chromatography (SHIMADZU GC-MS QP 2010SE equipped with a flame ionization detector and a Rtx-5MS capillary column, 330 ºC isotherms).

***Recycling Experiments*:** As for the recycling experiments, benzylic alcohol was used as the substrate. The TEMPO-CMP catalyst was separated from the reaction system by centrifugation for recycling, washed with excessive of methanol, and dried under vacuum. The catalyst was then reused in the next round of oxidation reactions without further activation.

Section 2. Synthetic Procedures



Scheme S1. Synthetic routes of compounds **1~4**.

5-methyl-N,N'-dicarbazolyl-1,3-benzene (5)[S1]

To a mixture of carbazole (5.4 g, 32 mmol), 3,5-dibromotoluene(4.0 g, 16 mmol), $Pd_2(dba)_3$ (586 mg, 0.044 mmol), di-tert-butyl-o-biphenyl phosphine (XPhos) (610 mg, 2.05 mmol) and sodium tert-butoxide (6.9 g, 69.82 mmol) was added toluene (160 mL) under N_2 atomosphere. The mixture was heated at 120 °C overnight. The reaction mixture was cooled to room temperature and filtered through celite. The filtrate was collected and evaporated under vacuum. The residue was then redissolved in methylene chloride. The organic phase was washed with water and brine and was dried over anhydrous Na_2SO_4. After the solvent was evaporated, a crude product was obtained and purified by column chromatography on silica gel, eluting with methylene chloride and petroleum ether (1:20, v/v) to give compound **5** (5.12 g, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16 (d, 4H, J=7.6 Hz), 7.62 (s, 1H), 7.55 (s, 2H),

7.52 (d, 4H, J=7.6 Hz), 7.45(t, 4H, J=7.2 Hz), 7.31(t, 4H, J=7.2 Hz), 2.60 (s, 3H).

5-bromomethyl-N,N'-dicarbazolyl-1,3-benzene (6)[S1]

A mixture of **5** (5.0 g, 11.8 mmol), NBS (2.52 g, 1.18 mmol), and benzoyl peroxide (286 mg, 1.18 mmol) in CCl_4 (120 mL) was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was collected and evaporated in vacuum. The residue was redissolved in methylene chloride and washed with water and dried over Na_2SO_4. The solvent was evaporated to dryness and afford the crude product, which was further purified by column chromatography on silica gel, eluting with petroleum ether to provide the desired product **6** (2.72 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.17 (d, 4H, J=7.6 Hz), 7.78 (s, 1H), 7.74 (s, 2H), 7.56 (d, 4H, J=7.6 Hz), 7.48 (t, 4H, J=7.2 Hz), 7.35 (t, 4H, J=7.2 Hz), 4.67 (s, 2H).

5-carboxyl-N,N'-dicarbazolyl-1,3-benzene (7)

To a mixture of compound **5** (4.0 g, 9.47 mmol), $KMnO_4$ (12.0 g, 75.9 mmol), 20% KOH (12 mL) was added pyridine (40 mL), and the reaction mixture was heated to reflux for 48 h. The reaction mixture was then cooled to room temperature and filtered. The filtrate was acidified by adding HCl (till pH = 3) and further extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The organic phase was evaporated to dryness, and further purified via column chromatography on silica gel (eluent: methylene chloride/petroleum ether (1:10, v/v)) to afford the desired product **7** (2.77 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (s, 2H), 8.18 (d, 4H, J=7.6 Hz), 8.10 (s, 1H), 7.56 (d, 4H, J=7.6 Hz), 7.49 (t, 4H, J=7.2 Hz), 7.36 (t, 4H, J=7.2 Hz).

1,3-dicarbazole-O-TEMPO (1) [S2]

To a solution of 4-hydroxy-TEMPO (104 mg, 0.6 mmol) in toluene (10 mL), Bu_4NBr (10 mg, 0.031 mmol) was added followed by **6** (300 mg, 0.6 mmol) and 50% NaOH (20 mL). The mixture was heated at 70 °C for 10 h. After cooling to room temperature, toluene and water were added. The aqueous layer was separated and extracted with ethyl acetate. The organic layers were combined and evaporated. The residue was purified by column chromatography using methylene chloride and petroleum ether (7:3, v/v) as eluent to afford the desired compound **1** (218 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ (ppm) 8.13 (m, 4H), 7.70 (m, 2H), 7.64 (m, 1H,), 7.52 (m, 4H), 7.43 (m, 4H), 7.30 (t, 4H, J=7.2 Hz), 4.76 (s, 2H), 3.86 (s, 1H), 2.10 (m, 2H), 1.74(m, 2H), 1.29 (m, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ (ppm) 151.38, 140.59, 139.40, 129.25, 128.85, 128.37,

126.94, 126.19, 124.42, 123.62, 120.77, 120.50, 120.37, 119.52, 112.18, 109.74, 109.67, 44.18, 21.51.

1,3-dicarbazole-NH-TEMPO (2) [S3]

Compound **6** (1.0 g, 2.0 mmol) and 4-amino-TEMPO (1.0 g, 5.84 mmol) was dissolved in toluene (150 mL) and added 2 mL Et_3N. The mixture was heated for 24 h at 100 °C. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether (1:5, v/v) as eluent to afford compound **2** (441 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ (ppm) 8.12 (m, 4H), 7.69 (s, 2H), 7.65 (s, 1H), 7.51 (m, 4H), 7.44 (m, 4H), 7.31 (m, 4H), 4.06 (s, 2H), 3.02 (s, 1H), 1.96 (m, 2H), 1.42(m, 2H), 1.23 (m, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ (ppm) 151.24, 140.63, 129.25, 128.84, 128.37, 126.92, 126.17, 125.31, 123.61, 120.74, 120.50, 120.43, 120.34, 119.49, 112.15, 109.74, 109.66, 45.62, 20.39.

1,3-dicarbazole-COO-TEMPO (3) [S4]

A mixture of 4-hydroxy-TEMPO (210 mg, 1.21 mmol), DCC (251 mg, 1.21 mmol), DMAP (13.3 mg, 0.11 mmol), and the carboxylic acid **7** (500 mg, 1.1 mmol) in 4 mL of anhydrous CH_2Cl_2 was stirred at room temperature. After the substrate was consumed (checked by TLC), 20 mL H_2O was added, and the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and concentrated by vacuum to obtain crude products, which was purified by the flash chromatography from mixture solvent petroleum ether and ethyl acetate (10:1, v/v) to afford the desired product **3** (412 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ (ppm) 8.35 (s, 2H), 8.16 (d, 4H, J=7.6 Hz), 8.03 (s, 1H), 7.52 (m, 4H), 7.46 (m, 4H), 7.30 (m, 4H), 5.39 (s, 1H), 2.16 (m, 2H), 1.93 (m, 2H), 1.35 (m, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ(ppm) 164.72, 151.18, 140.45, 139.79, 134.21, 129.42, 129.25, 128.38, 126.61, 126.42, 123.82, 120.74, 119.54, 112.19, 109.53, 68.48, 60.11, 43.67, 20.84.

1,3-dicarbazole-CONH-TEMPO (4) [S5]

4-amino-TEMPO (520 mg, 3 mmol) was first dissolved in toluene (30 mL) and then added Et_3N (0.9 mL). The reaction mixture was cooled in a water bath (15 °C) and a solution of 5-acylchloride -*N,N'*-dicarbazolyl-1,3-benzene (prepared from **7** (1.356 g, 3 mmol) and oxalyl chloride (0.3 mL, 3.3 mmol) in toluene (30 mL)) was added dropwise. After 2 h, DCM (45 mL) and 1 N aq. HCl (30 mL) were added and the mixture was left stirring for 5 min. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered and evaporated to dryness in vacuo. The residue was

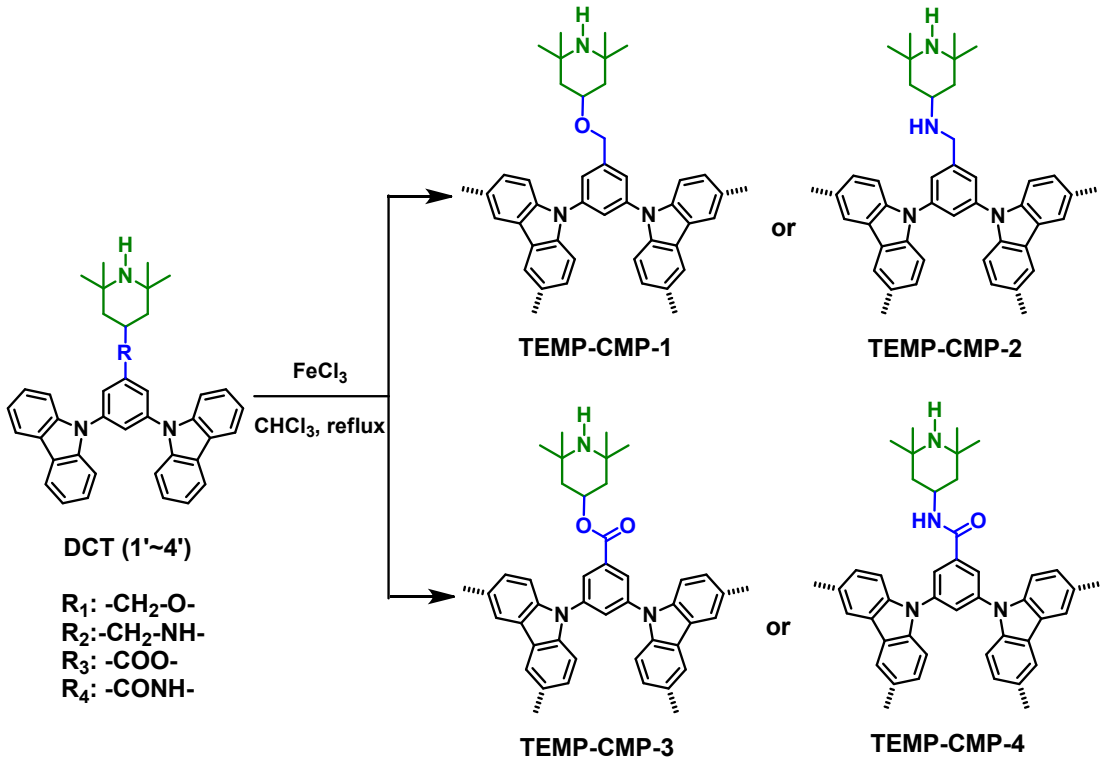
further purified by the flash chromatography (eluent: petroleum ether and ethyl acetate (4:1, v/v)) to afford the product **4** (1.29 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ (ppm) 8.12 (m, 4H), 7.96 (s, 1H,), 7.52 (m, 4H), 7.43 (m, 4H), 7.31 (m, 4H), 6.46 (s, 1H), 4.49 (s, 1H), 2.02 (m, 2H), 1.75 (m, 2H), 1.26(s, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, phenylhydrazine): δ (ppm) 165.14, 151.51, 140.47, 139.91, 138.25, 129.24, 128.38, 128.07, 126.42, 124.28, 123.80, 120.75, 120.62, 119.57, 112.23, 109.61, 60.64, 53.49, 44.55, 19.96.

Polymerization Procedures [S6]

The TEMPO-based monomer (30 mg) was dissolved in 5 mL of anhydrous chloroform and then added dropwise to a suspension of ferric chloride (66 mg) in 3 mL of anhydrous chloroform. The mixture was heated to reflux for 24 h under nitrogen atmosphere. The reaction mixture was quenched by adding 15 mL methanol. The resulting mixture was kept stirring for another one hour and the precipitate was collected by filtration. After washed with methanol, the obtained solid was stirred vigorously in hydrochloric acid solution (37%) for 2 h. The suspension was then filtered and washed with water and methanol and dried in vacuum to afford the corresponding TEMPO-CMPs with good yields (90% for TEMPO-CMP-**1**, 87% for TEMPO-CMP-**2**, 92% for TEMPO-CMP-**3**, 92% for TEMPO-CMP-**4**.). The Fe residual contents were determined to be 0.23%, 0.26%, 0.15% and 0.15% for TEMPO-CMP-**1**~**4**, respectively by ICP-MS techniques using Agilent 7700X ICP-MS model.

Preparation of 1'~4':

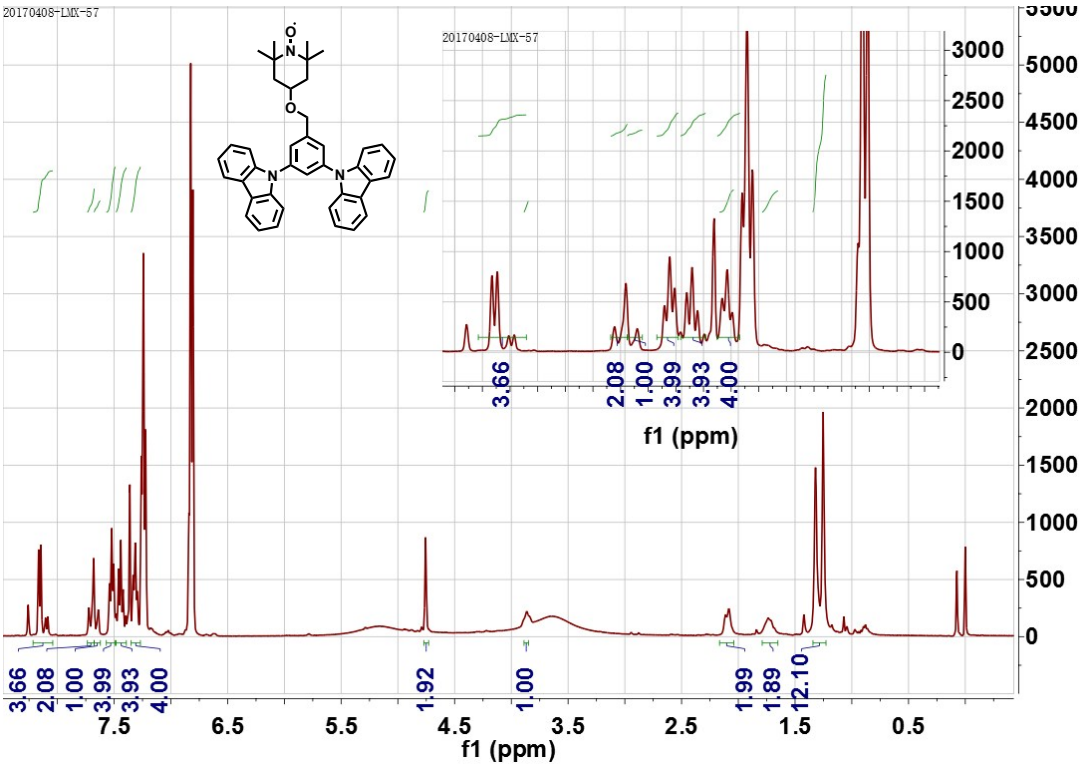
As shown in Scheme S2, the control CMP samples TEMP-CMPs were prepared in the same reaction conditions while using **1'~4'** as the monomer. And the monomers were synthesized with reference to the synthesis of molecules **1**～**4**, using 4-hydroxy-TEMP and 4-amino-TEMP instead of 4-hydroxy-TEMPO and 4-amino-TEMPO. The yields are 73%, 59%, 42%, 81% respectively.

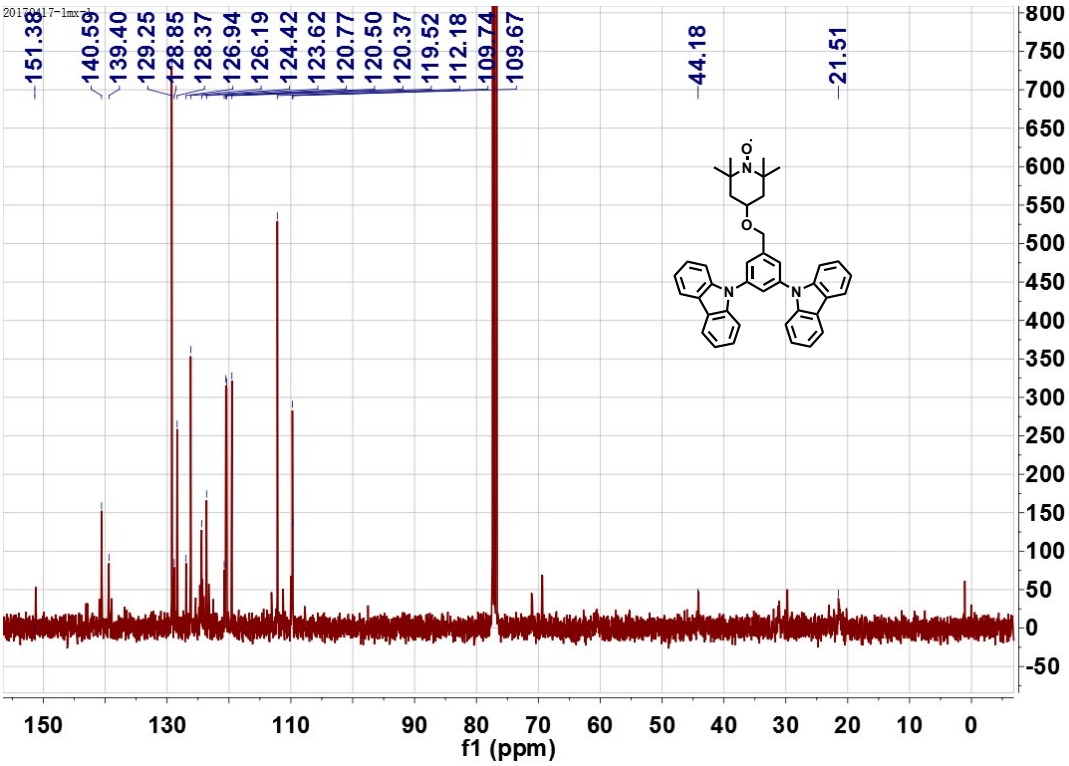


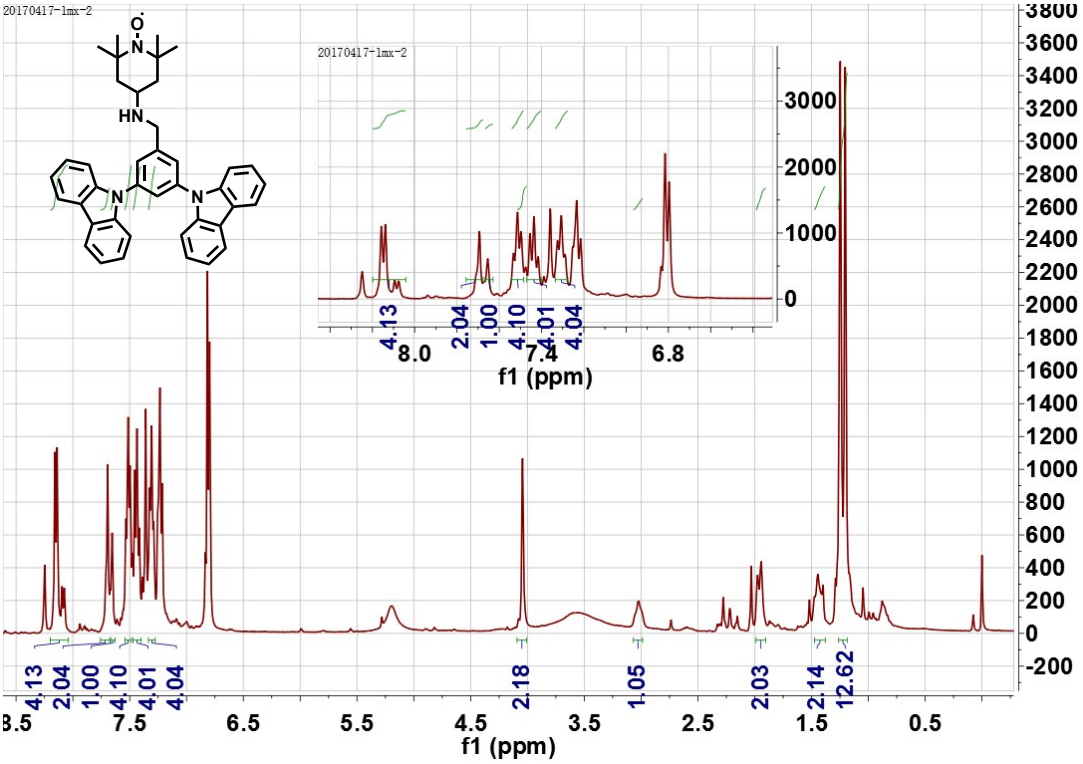
Scheme S2. Synthetic routes of the four TEMP-CMPs for comparison and solid state NMR measurement.

Section 3. ^{1}H NMR and ^{13}C NMR Spectra for TEMPO Monomers

As a result of the existence of free radicals, NMR can't be measured, therefore, adding suitable amount of phenylhydrazine to $CDCl_3$ to stabilize free radicals. The NMR data of phenylhydrazine are listed below: ^{1}H NMR(400 MHz, $CDCl_3$): δ (ppm) 7.36 (s, 1H), 7.24 (m, 2H), 6.82 (m, 2H), 5.17 (broad, 1H), 3.57 (broad, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 151.24, 129.25, 119.50, 112.14.



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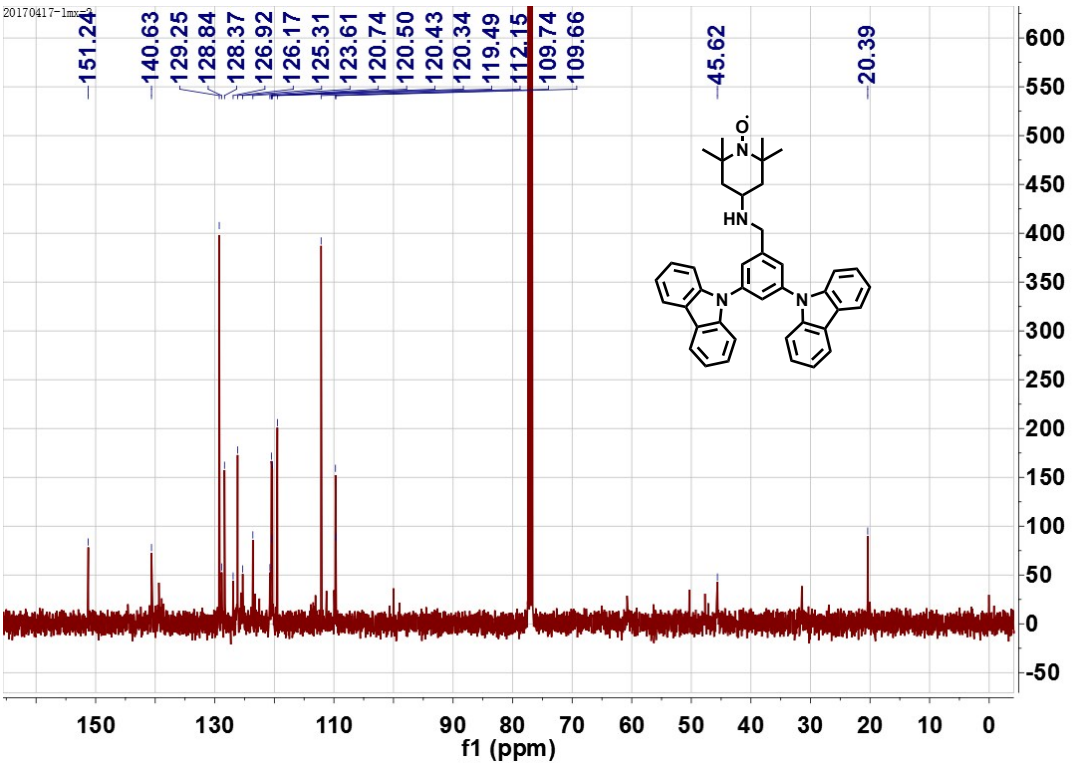
2.04
1.00
4.10
4.01
4.04
2.18
1.05
2.03
2.14
12.62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f1 (ppm)
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140.63
129.25
128.84
128.37
126.92
126.17
125.31
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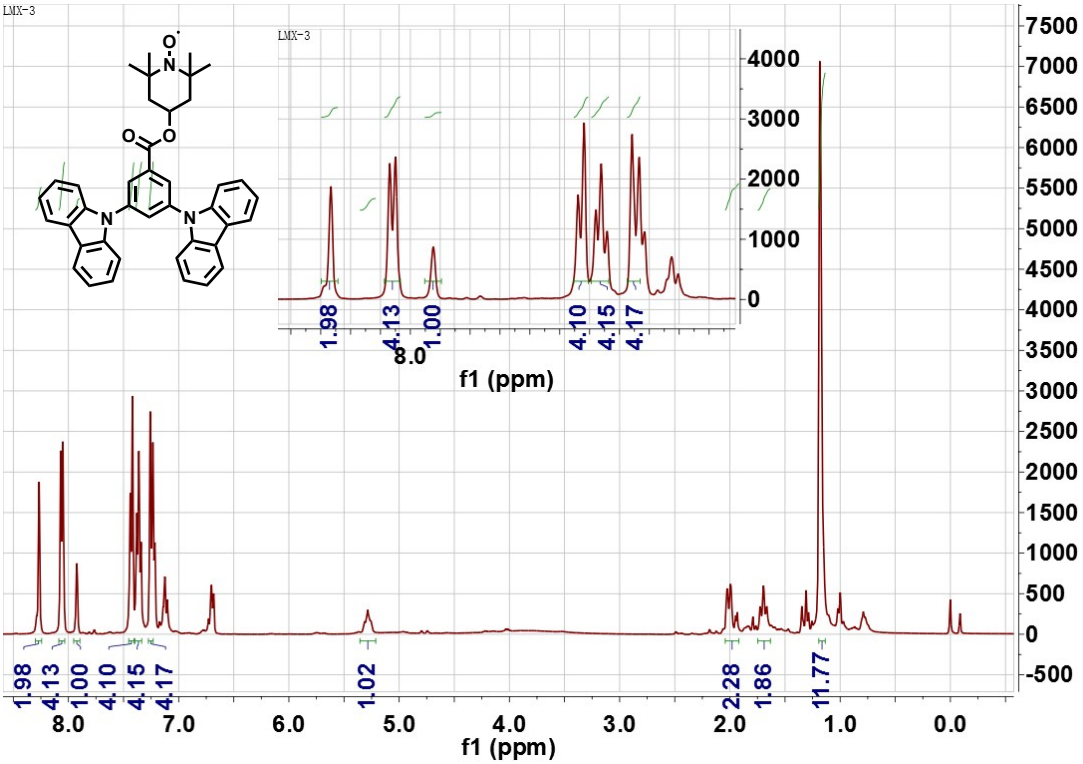
112.15
109.74
109.66
45.62
20.39


LMX-3
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1.00
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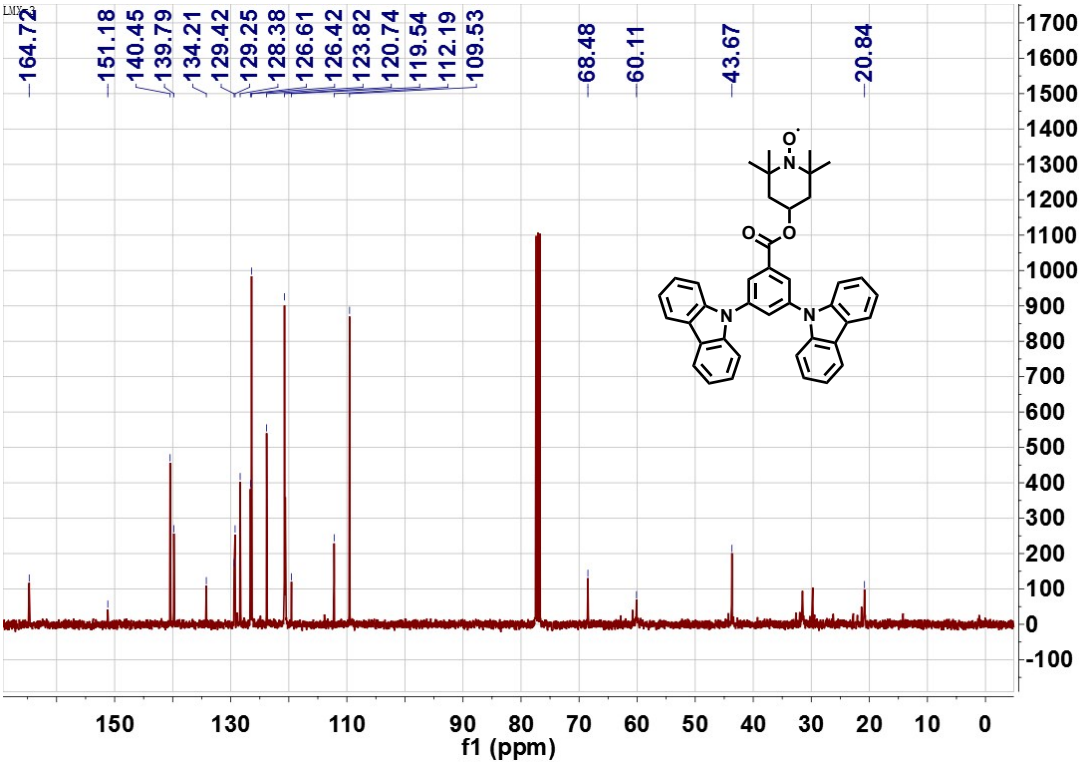
4.17
1.02
2.28
1.86
11.77
f1 (ppm)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43.67
20.84
f1 (ppm)

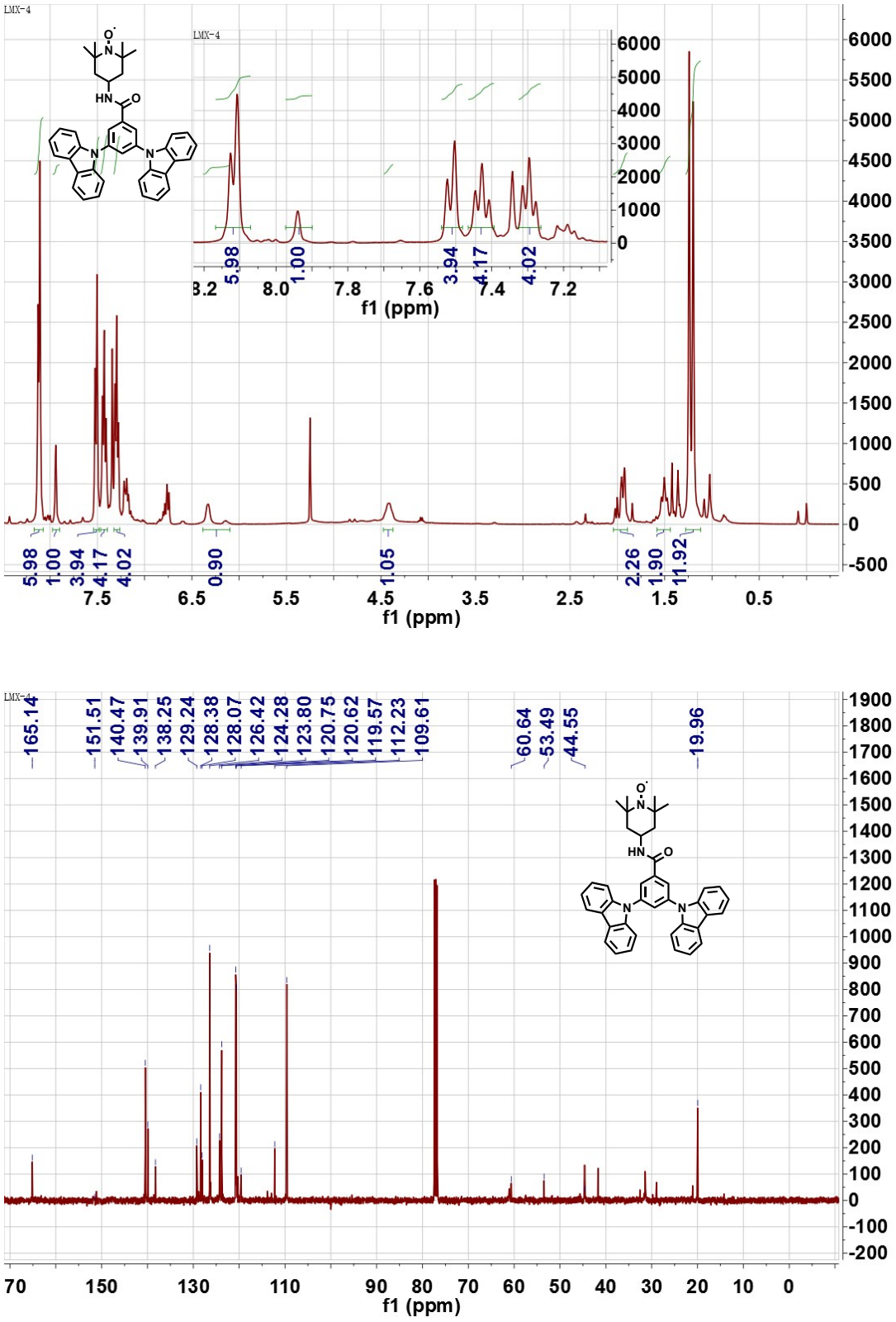


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (400 MHz, $CDCl_3$) spectra of carbazole functionalized TEMPO monomers **1~4**.

Section 4. Solid State ^{13}C CP/MAS NMR Spectra

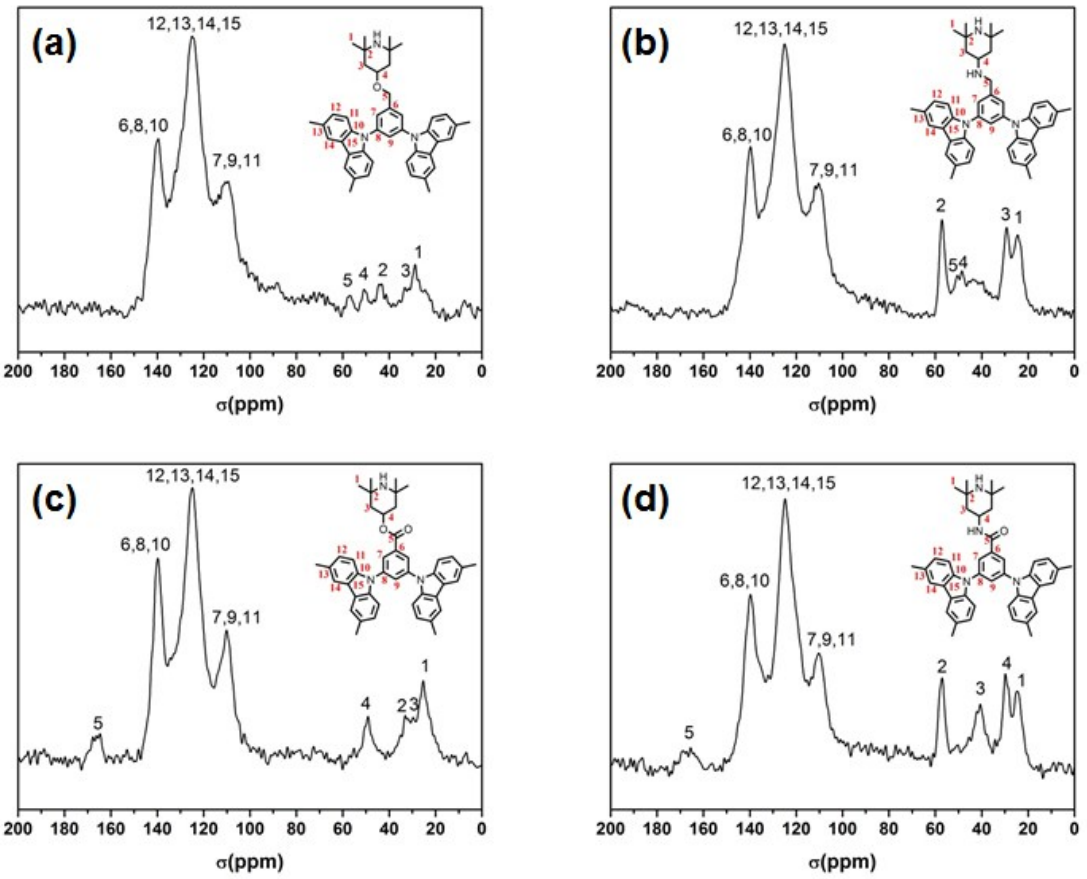


Figure S2. Solid state ^{13}C CP/MAS NMR spectra of (a) **TEMP-CMP-1,** (b) **TEMP-CMP-2,** (c) **TEMP-CMP-3** and (d) **TEMP-CMP-4**.

Section 5. Solid State EPR Spectra

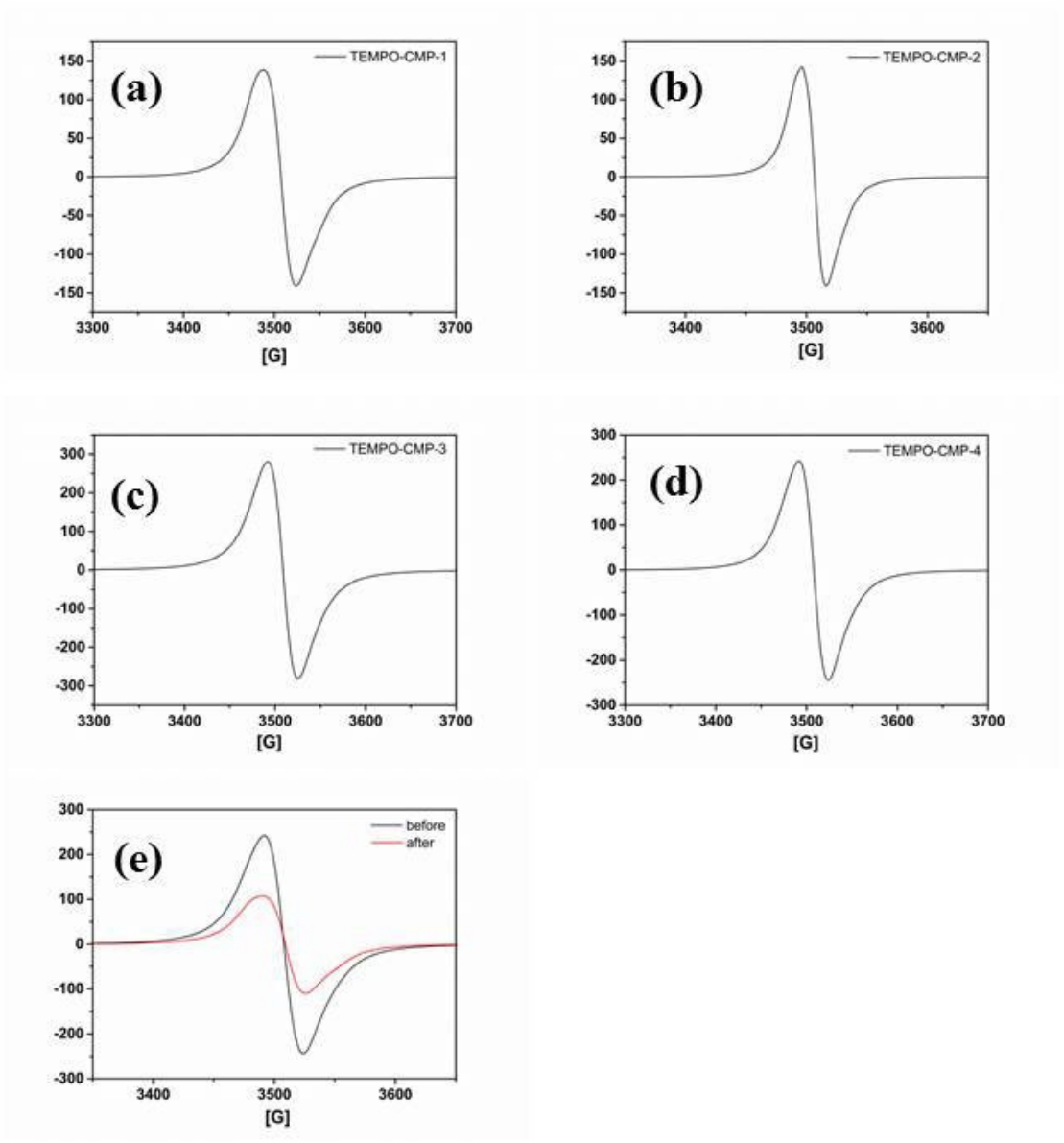


Figure S3. Electron paramagnetic resonance (EPR) spectra of (a) **TEMPO-CMP-1**, (b) **TEMPO-CMP-2**, (c) **TEMPO-CMP-3**, (d) **TEMPO-CMP-4**, and (e) comparison of EPR of **TEMPO-CMP-4** before and after the ten times recycling catalysis experiment.

Section 6. FT-IR Spectra

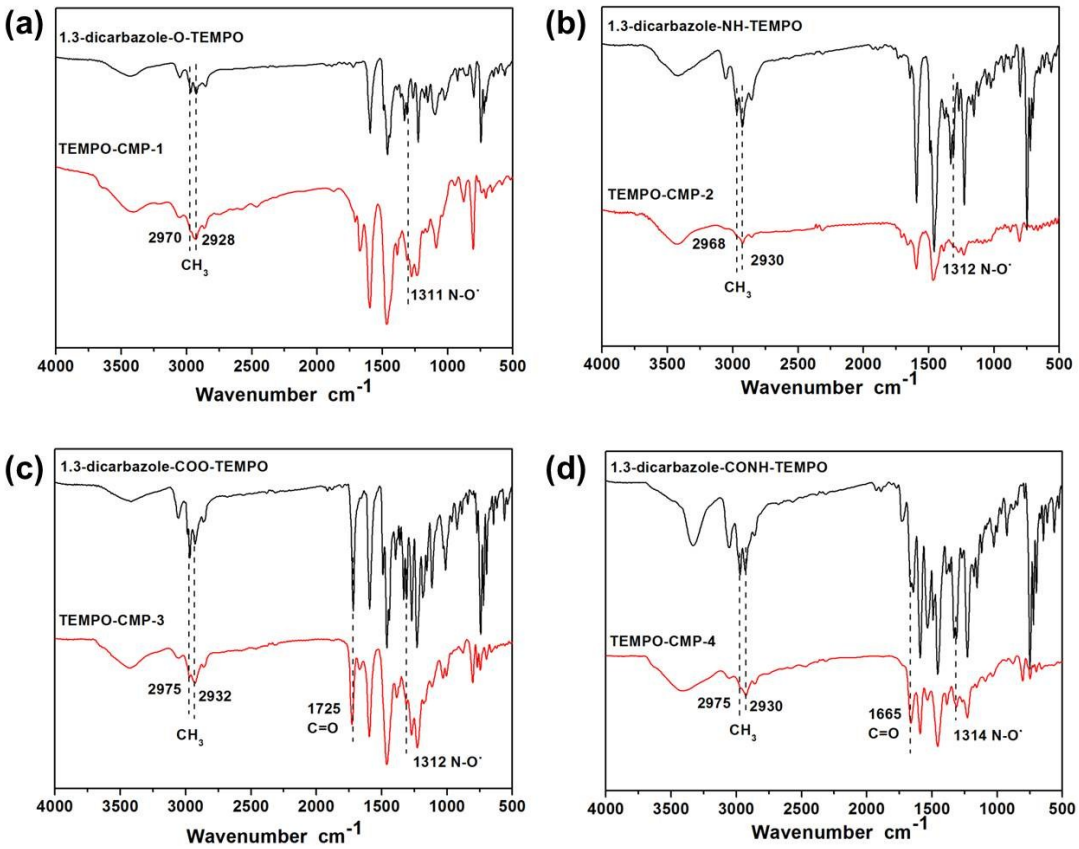


Figure S4. FT-IR spectra comparison of **TEMPO-CMPs** (red line) and corresponding TEMPO-based dicarbazole monomers (black line). (a) **TEMPO-CMP-1**; (b) **TEMPO-CMP-2**; (c) **TEMPO-CMP-3**; (d) **TEMPO-CMP-4**.

Section 7. Elemental Analysis

Table S1. Elemental analysis of **TEMPO-CMPs**

	N%	C%	H%
TEMPO-CMP-1	4.60	62.91	4.82
TEMPO-CMP-2	3.79	56.02	7.90
TEMPO-CMP-3	4.34	45.91	9.08
TEMPO-CMP-4	7.10	66.78	5.77

Section 8. Porosity Data

Table S2. Porosity Data of the **TEMPO-CMPs**

	S_{BET} (m^2/g)	pore volume (m^3/g)	Pore diameter (nm)
TEMPO-CMP-1	495	0.45	1.62
TEMPO-CMP-2	357	0.33	2.33
TEMPO-CMP-3	603	0.54	1.40
TEMPO-CMP-4	836	0.62	1.72

Section 9. Thermogravimetric Analysis

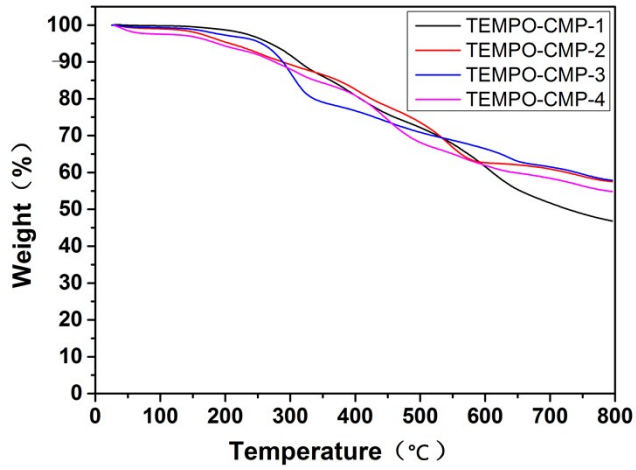


Figure S5. Thermogravimetric analysis for **TEMPO-CMP-1** (black), **TEMPO-CMP-2** (red), **TEMPO-CMP-3** (blue) and **TEMPO-CMP-4** (pink).

Section 10. PXRD Profiles

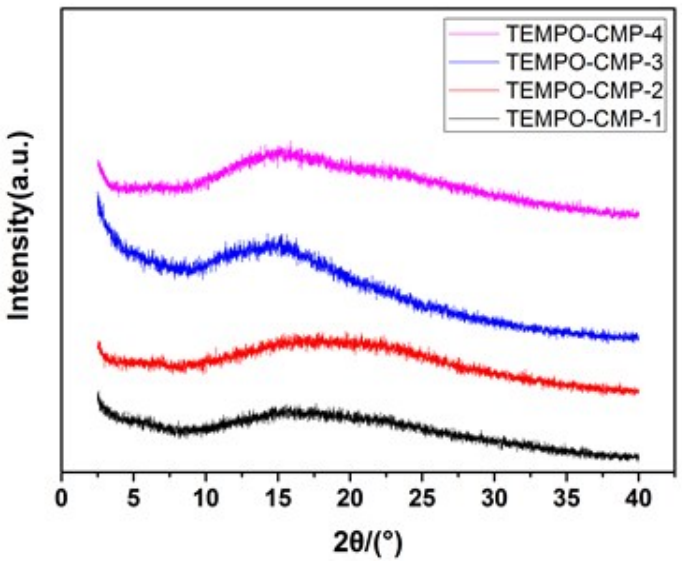


Figure S6. Powder X-ray diffraction profiles of **TEMPO-CMPs** (black line for **TEMPO-CMP-1**, red line for **TEMPO-CMP-2**, blue line for **TEMPO-CMP-3**, pink line for **TEMPO-CMP-4**).

Section 11. SEM & TEM Images

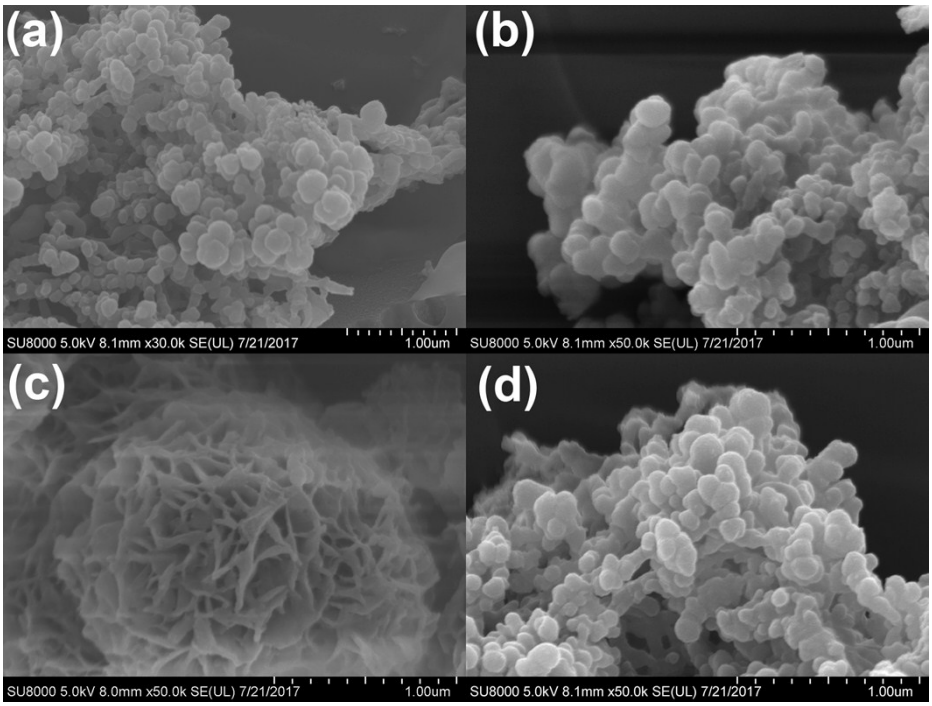


Figure S7. SEM images of **TEMPO-CMPs** (a) for **TEMPO-CMP-1**, (b) for **TEMPO-CMP-2**, (c) for **TEMPO-CMP-3**, (d) for **TEMPO-CMP-4**.

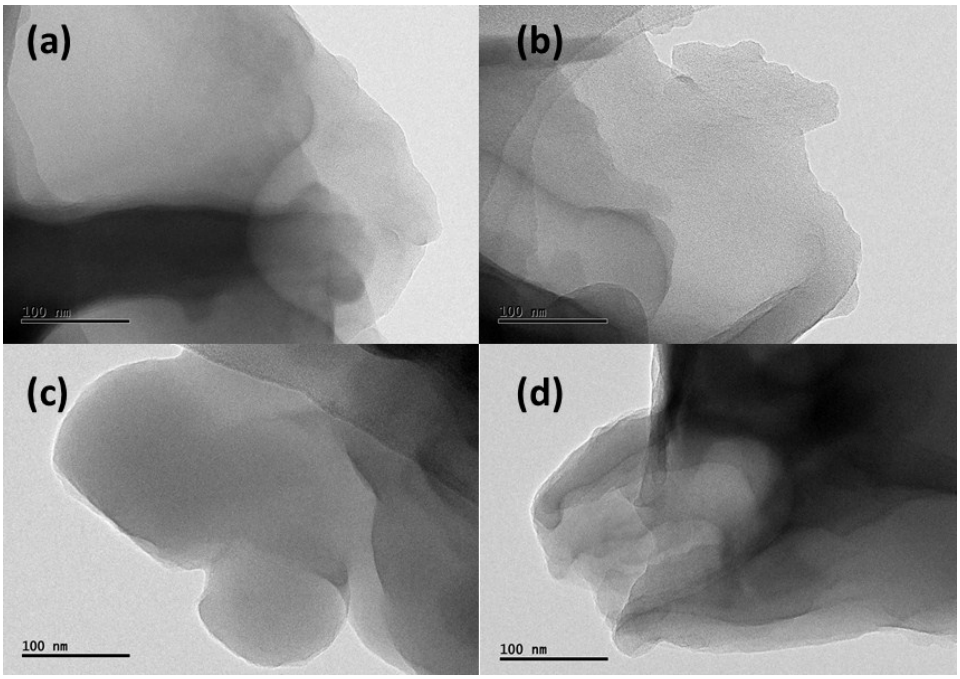


Figure S8. TEM images of **TEMPO-CMPs** (a) for **TEMPO-CMP-1**, (b) for **TEMPO-CMP-2**, (c) for **TEMPO-CMP-3**, (d) for **TEMPO-CMP-4**.

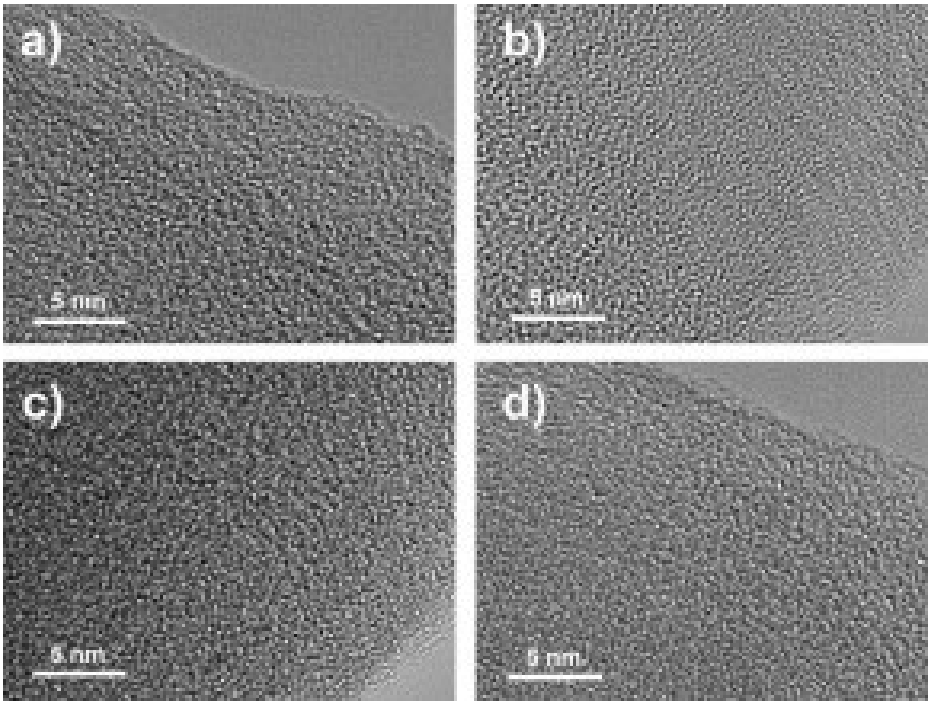


Figure S9. HR-TEM images of **TEMPO-CMPs** (a) for **TEMPO-CMP-1**, (b) for **TEMPO-CMP-2**, (c) for **TEMPO-CMP-3**, (d) for **TEMPO-CMP-4**.

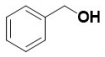
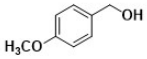
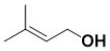
Section 12. Comparison Table of Catalytic Performance

Table S3. Comparison of catalytic activities on oxidation of benzyl alcohol

Cat (mol%)	Yield (%)	TOF (h^{-1})	Ref.
TEMPO	> 99	100	*J. Am. Chem. Soc.* **2004**, *126*, 4112−4113
TEMPO@SBA-15	99	66.7	*Angew. Chem. Int. Ed.* **2007**, *46*, 7210–7213
TEMPO@Fe_3O_4	> 99	20	*Chem. Eur. J.*, **2010**, *16*, 12718-12726
[BMIm]Br/ TEMPO@SBA-15	> 99	28.57	*Org. Biomol. Chem.* **2011**, *9*, 4194–4198
DPIO	94	1.1	*J. Am. Chem. Soc.* **2014**, *136*, 7543-7546
SABNO	> 99	111.1	*ChemSusChem* **2014**, *7*, 2735-2741
MNST 1	100	125	*Chem. Eur. J.* **2011**, *17*, 6056-6060
TEMPO-CMP-4	> 99	333.3	**our work**

Section 13. Catalytic Performance of TEMPO Monomer

Table S4. Aerobic oxidation of alcohols using DCT-4[a]

Entry	Substrate	time (h)	Conv.[b] (%)	Sele.[b] (%)
1		1	99	97
2		1	99	98
3		4	51	99
4		5	33	98

[a]Reaction conditions: 0.3 mmol of alcohol, 9.7 mg of DCT-4 (5 mol% of nitroxide radical), 4.2 mg of $NaNO_2$ (20 mol%), 4.3 mg of DBDMH (5 mol%) in 0.4 mL of CH_3COOH with an O_2 balloon at room temperature. [b]Conversion and selectivity were determined by GC.

Section 14. Chemical Stability Studies of TEMPO-CMPs

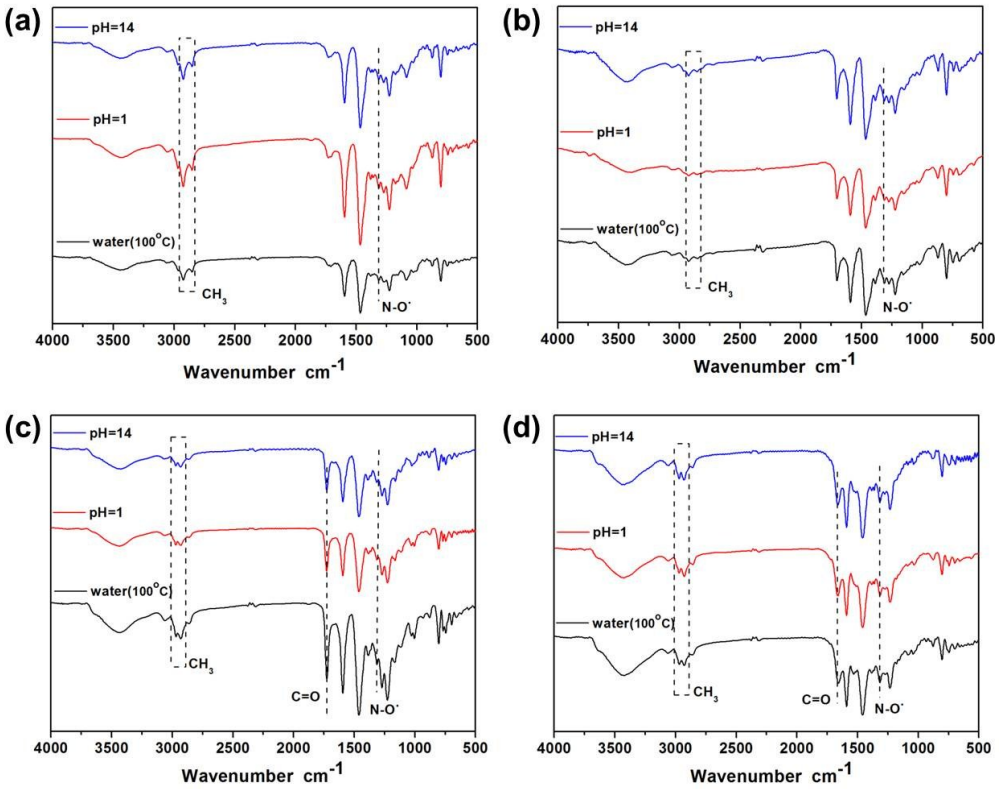


Figure S10. FT-IR spectra of **TEMPO-CMPs** after treatment with boiling water (100 °C) (black line), 0.1 M HCl (pH = 1) aqueous solution (red line) and 0.1 M NaOH (pH = 14) aqueous solution (blue line) for 24 h: (a) **TEMPO-CMP-1**; (b) **TEMPO-CMP-2**; (c) **TEMPO-CMP-3**; (d) **TEMPO-CMP-4**

Section 15. Cycling Stability Studies of TEMPO-CMP-4

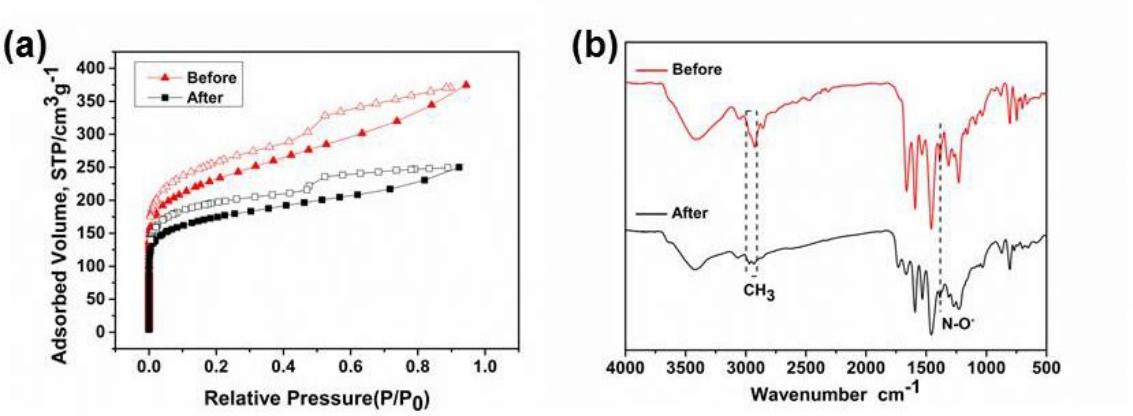


Figure S11. (a) Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K and pore size distribution (inset) based on NLDFT calculation for **TEMPO-CMP-4** before (red) and after (black) 20 times recycling experiments. The BET surface areas were calculated to be 648 $m^2 g^{-1}$, slightly lower compared with the as synthesized sample (836 $m^2 g^{-1}$). (b) FT-IR spectra of **TEMPO-CMPs** before (red) and after (black) 20 times recycling experiments.

Section 16. Supporting References

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