Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI) for:

Quinone-amine polymer as the metal-free and reductant-free catalyst for hydroxylation of benzene to phenol with molecular oxygen

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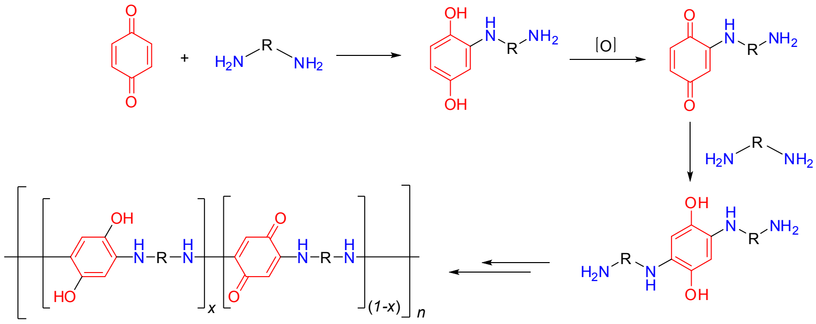
1. Characterization

Fourier transform infrared spectroscopy (FT-IR) was performed on a VECTOR-22 using the KBr pellet technique with a resolution of 2 cm^{-1} from 400 to 4000 cm^{-1} and consisted of 32 scans at room temperature. Element analysis (C, H, N) was carried out on Elemeraor VarioELIII. BET surface area of the catalyst was conducted by the adsorption of N_2 at -196 ^oC (Gemini VII 2.00, Micromeritics Instrument Corporation). The X-Ray Diffraction (XRD) patterns were obtained by an X-ray diffractometer (Rigaku IV) operated with Cu-Kα radiation at 40 kV and 40 mA, scanning mode of 2 theta/theta, scanning type of continuous scanning, and a scanning range from 3^o to 90^o at a scanning rate of 8 ^{o}/min. The X-ray photoelectron spectrometer (XPS) was carried out at 15 kV and 8 mA, with the binding energies calibrated at 284.6 eV from C1s of the adventitious carbon. Asymmetrical XPS peaks were deconvoluted by using the curve-fitting approach with CasaXPS software, as well as by applying Shirley background subtraction and Lorentzian–Gaussian functions (30% L, 70% G). Scanning electron microscope (SEM) for the sample morphology was measured at 20 kV and 15 mA on the Hitachi S-4800. The solid state ^{13}C NMR was conducted on the Agilent 600M. The GPC was carried out on the Waters1525. The Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E500 spectrometer.

2. Scheme.

Scheme S1



Scheme S1. Synthesis of QAPs with benzoquinone and diamine.

3. Figures.

Figure S1

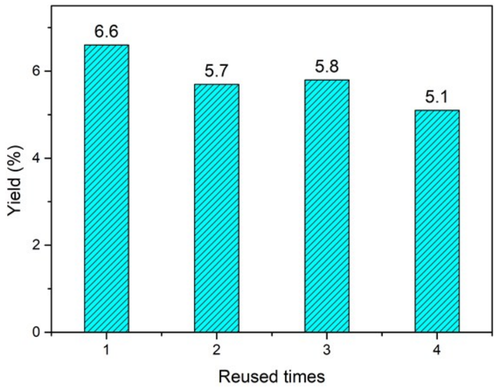


Fig. S1 The recycle of the QAP (ethylenediamine). Reaction condition: 0.5 mL benzene; 100 mg catalyst; 0.4 LiOAc; 3.0 mL 70%(V/V) acetic acid aqueous solution; temperature, 120 ^{o}C; O_2 pressure 2.0 MPa; reaction time, 12 h.

Figure S2

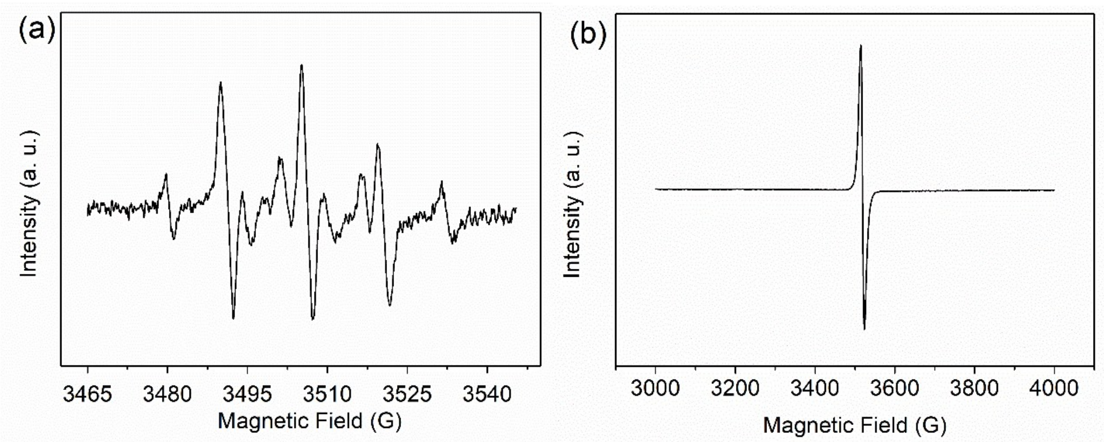
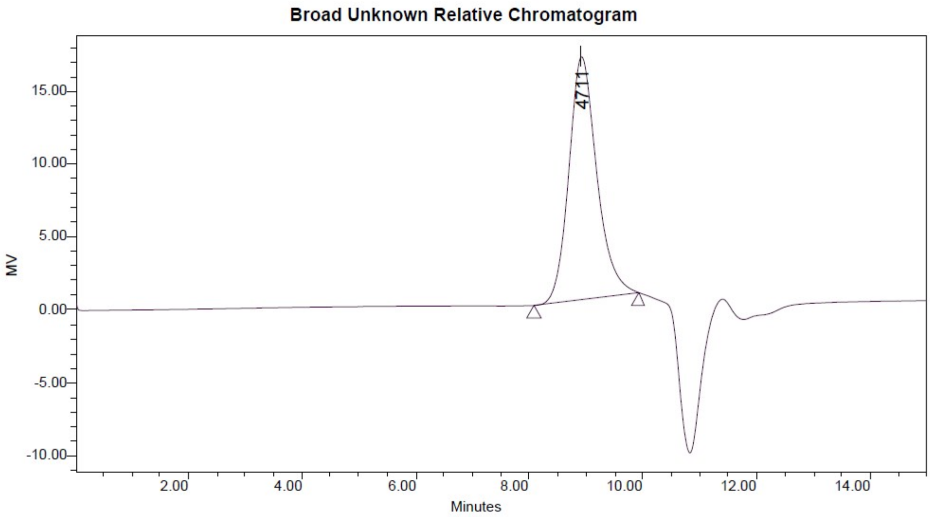


Fig. S2 The EPR spectra of (a) reaction solution, (b) the solid QAP (ethylenediamine). Reaction condition of (a): 100 mg catalyst; 0.4 LiOAc; DMPO, 0.5 mmol; 3.0 mL 70%(V/V) acetic acid aqueous solution; temperature, 50 ^{o}C; O_2 pressure 1 bar; reation time 5 min.

Figure S3



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		3664	4852	4711	6114	7483	1.324512	1.260061	1.542061

Fig. S3 The GPC image and the data of QAP (ethylenediamine).

Figure S4

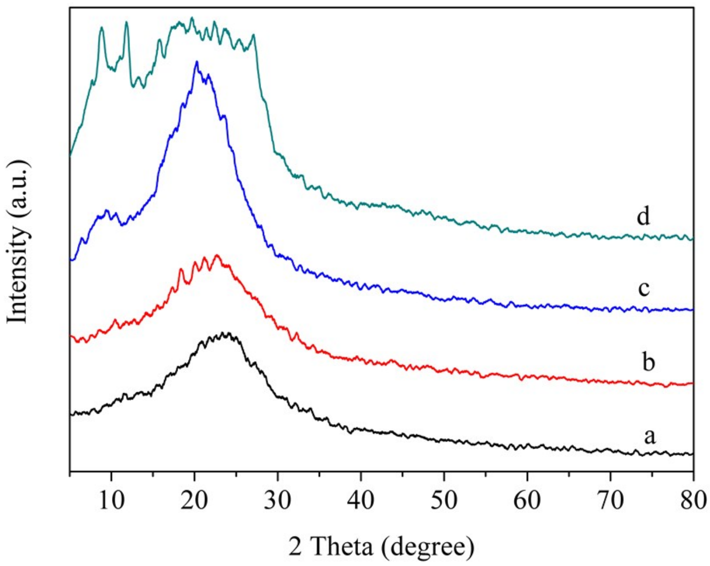


Fig. S4. The XRD spectra of different amine based QAP. (a) Ethylenediamine, (b) propanediamine, (c) hexanediamine, (d) *o*-phenylenediamine.

Figure S5

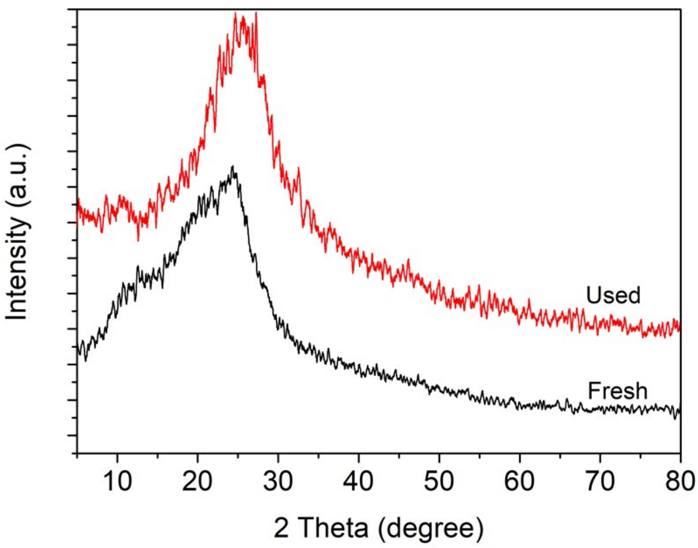


Fig. S5 The XRD spectra of QAP (ethylenediamine) before and after use..

Figure S6

There are two kinds of sphere in the QAP. One was an isolated large microsphere; the other was an interconnected smaller sphere.

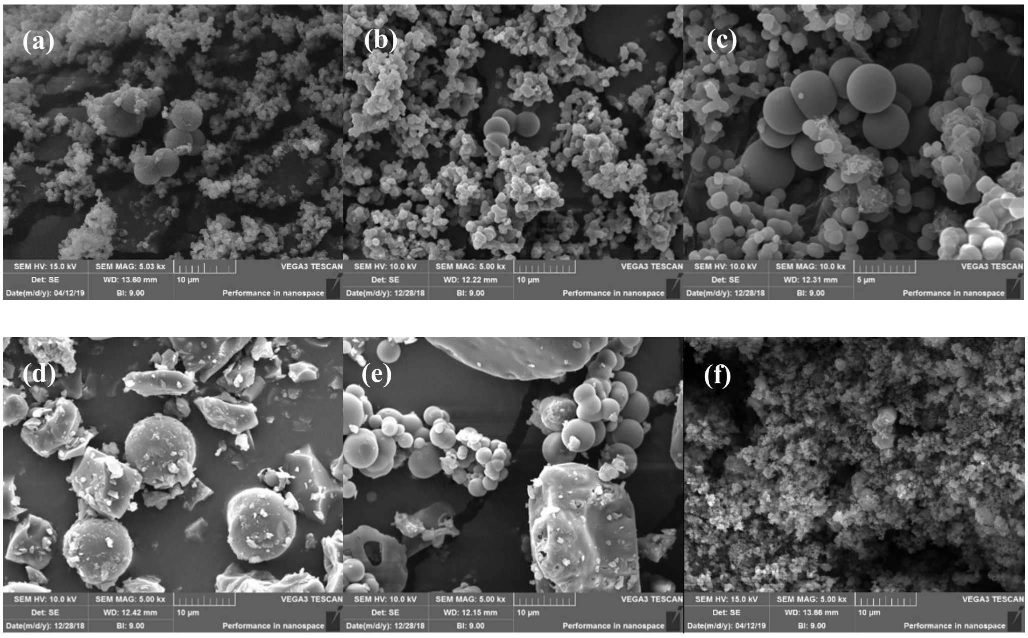


Fig. S6. The SEM images of different amine based QAP. (a) Ethylenediamine, (b) propanediamine, (c) hexanediamine, (d) *o*-phenylenediamine, (e) melamine, (f) used catalyst of ethylenediamine based QAP.

Figure S7

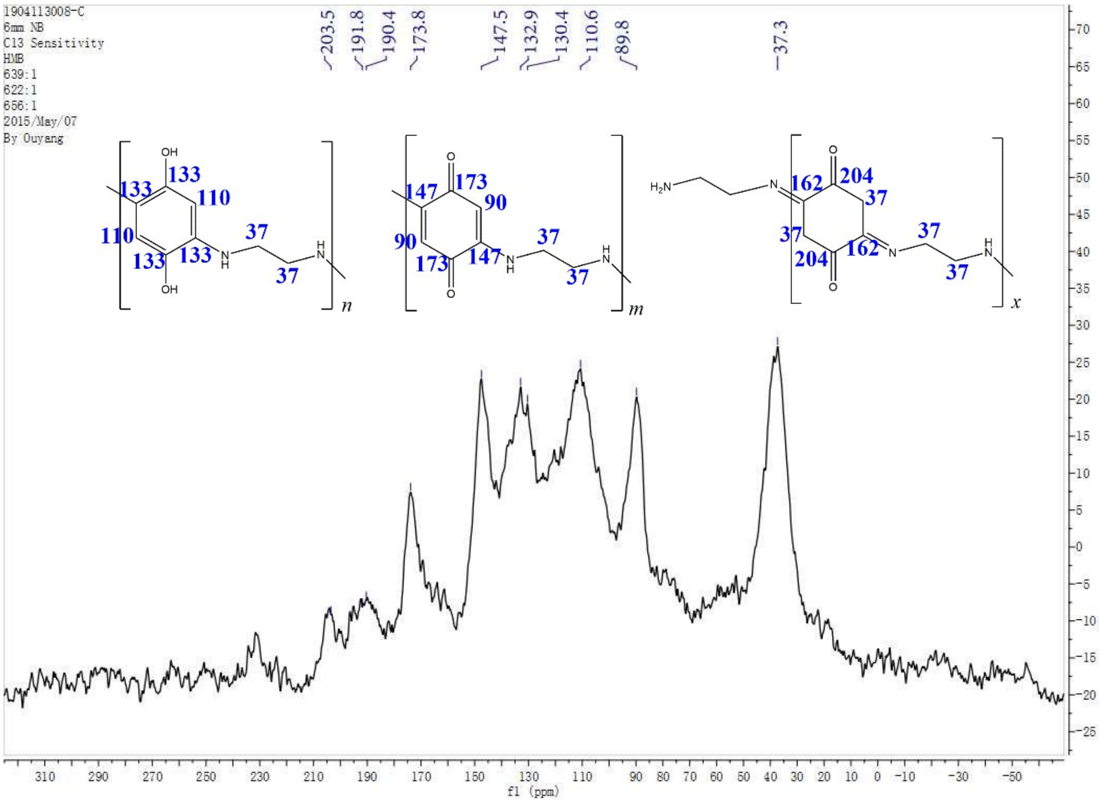


Fig. S7 Solid state ^{13}C NMR spectrum of QAP (ethylenediamine).

Figure S8

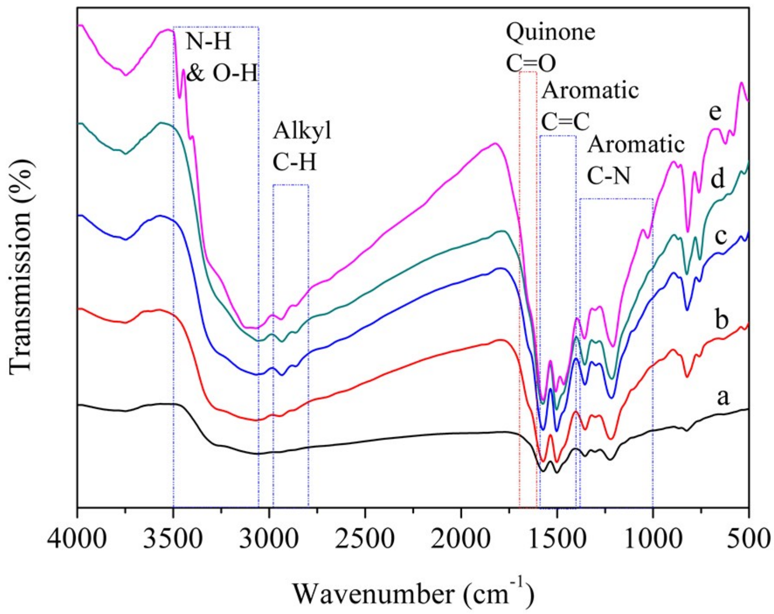


Fig. S8. The FT-IR spectra of different amine based QAP. (a) Ethylenediamine, (b) propanediamine, (c) hexanediamine, (d) *o*-phenylenediamine, (e) melamine.

Figure S9

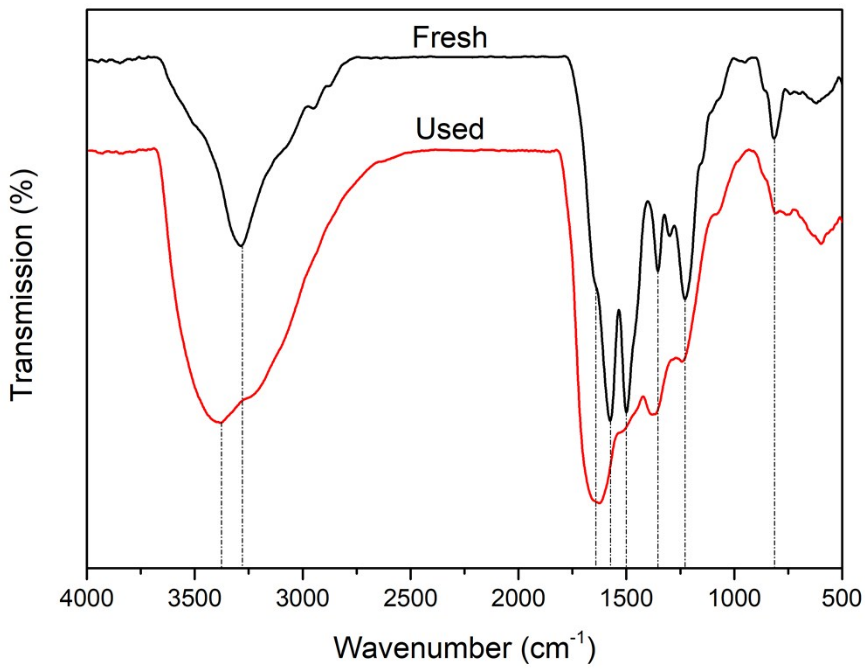


Fig. S9. The FT-IR spectra of QAP (ethylenediamine) before and after use.

Figure S10

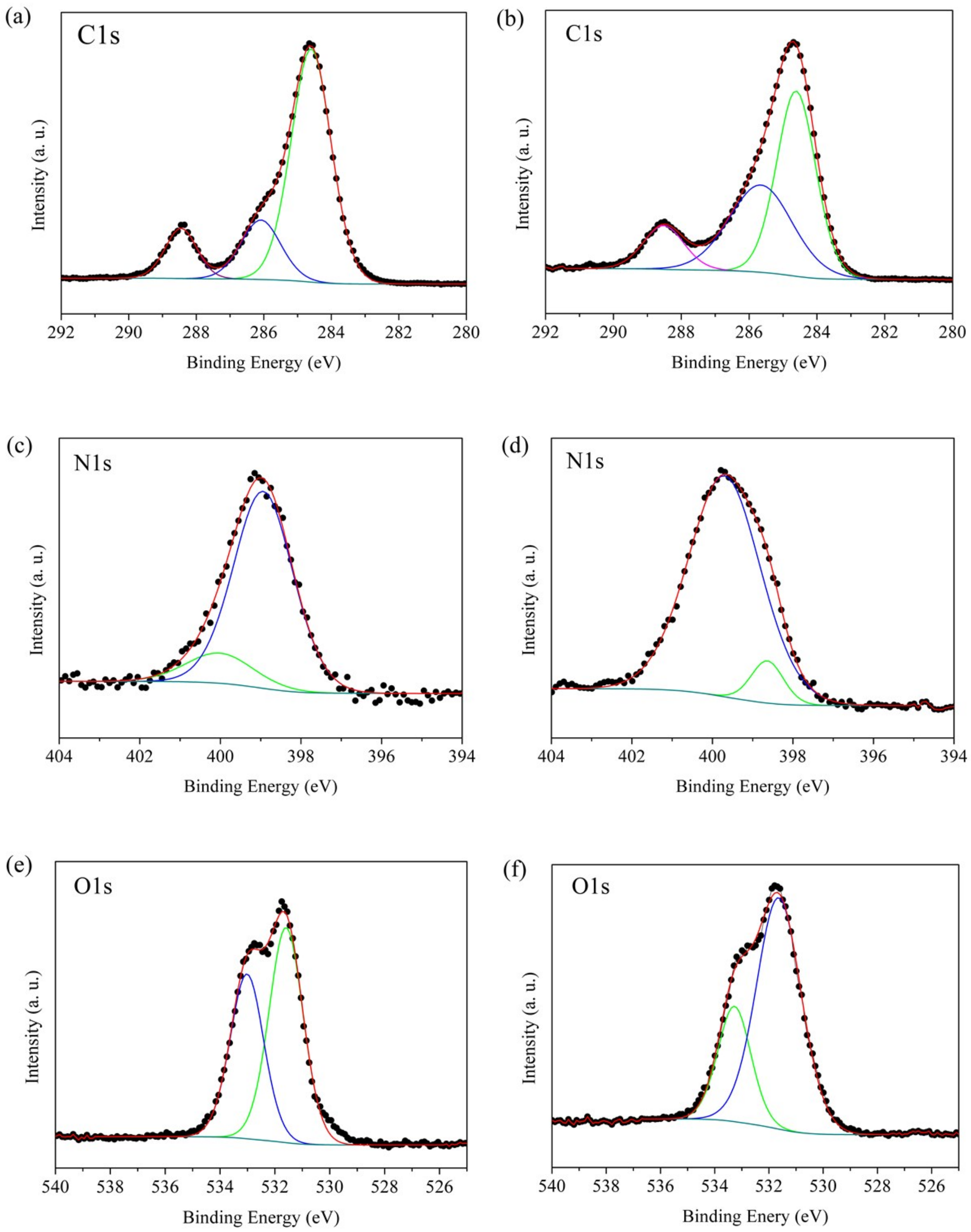


Fig. 10. The XPS spectra of ethylenediamine based QAP. (a), (c), and (e) are the fresh QAP. (b), (d), (f) are the used QAP.

Figure S11

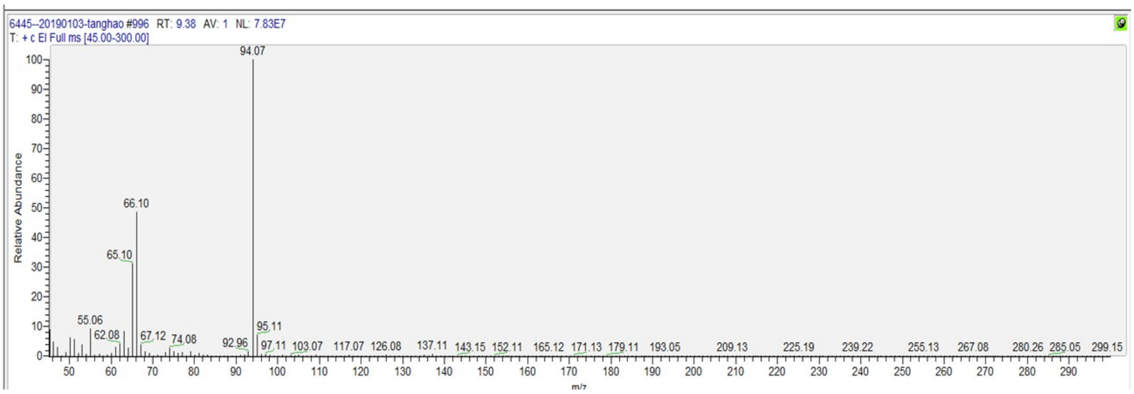


Fig. S11. The Mass spectrum of phenol.

4. Tables

Table S1

Table S1. Hydroxylation of benzene to phenol with O_2 on different catalysts.

Entry	Catalyst	Reducing agent	Temperature (℃)	Time (h)	Yield (%)	Ref.
1	V_xO_y@C	Ascorbic acid	80	24	12.2	[1]
2	V@CN	Ascorbic acid	105	11	23.0	[2]
3	L-Mn-PMoV	Ascorbic acid	100	10	14.4	[3]
4	V/SiO_2	Ascorbic acid	90	10	13.7	[4]
5	V/NH_2-SBA-15	Ascorbic acid	60	18	13.3	[5]
6	$CsPMoV_2$	Ascorbic acid	80	24	7.2	[6]
7	V–N–C-600	Ascorbic acid	80	24	12.6	[7]
8	V/UiO-66-NH_2	Ascorbic acid	60	21	22.0	[8]
9	$H_7PMo_8V_4O_{40}$	CO	90	15	27.3	[9]
10	$Pd(OAc)_2$+$H_5[PMo_{10}V_2O_{40}]$	None [a]	100	2	3.8	[10]
11	HMS–HPA(V_2) + $Pd(OAc)_2$	None [a]	120	10	9.2	[11]
12	C_3N_4-$PMoV_2$	None [a]	130	4.5	13.6	[12]
13	Pd-VO*x*	None [a]	140	5	5.2	[13]
14	$[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$	None [a]	120	4	9.8	[14]
15	VOC_2O_4-N-5	None [a]	150	10	4.0	[15]
16	$[DiBimCN]_2HPMoV_2$@NC-580	None [a]	140	17	10.5	[16]
17	FeC(5)	None [a]	150	30	14.2	[17]
18	Ch_5PMoV_2	None [a]	120	4.5	10.7	[18]
19	NOC-0.15	None [a]	150	48	12.5 [b]	[19]
20	Ethylenediamine based QAP	None [a]	120	24	13.1 [b]	This work
21	Propanediamine based QAP	None [a]	120	12	15.9 [b]	This work
22	Hexanediamine based QAP	None [a]	120	12	15.0 [b]	This work

[a] Reductant-free reaction.

[b] Reductant-free and metal-free reaction.

Table S2

Table S2 The effect of solvent on the hydroxylation of benzene to phenol [a]

Entry	Solvents	Yield (%)
1	70% (V/V) acetic acid	6.7
2	Acetonitrile	–
3	PEG-800	–

[a] Reaction condition: 0.5 mL benzene; 100 mg catalyst; 0.4 LiOAc; 3.0 mL solvent; temperature, 120 ^{o}C; O_2 pressure 2.0 MPa; reaction time, 12 h.

Table S3

Table S3 The controlled experiments on the hydroxylation of benzene to phenol [a]

Entry	Catalyst	Yield (%)
1	Hydroquinone	10.8
2	*p*-Benzoquinone	11.7

[a] Reaction condition: 0.5 mL benzene; 100 mg catalyst; 0.4 LiOAc; 3.0 mL70%(V/V) acetic acid aqueous solution; temperature, 120 ^{o}C; O_2 pressure 2.0 MPa; reaction time, 12 h.

Table S4

Table S4 The texture structures of different amines based QAP.

Catalyst	S_{BET} (m^2/g)	V_{pore} (cm^3/g)
Ethylenediamine based QAP	8.2110	0.0472
Propanediamine based QAP	2.0292	0.0050
Hexanediamine based QAP	2.6164	0.0125
o-Phenylenediamine based QAP	0.6369	0.0020
Melamine based QAP	0.6867	0.0029

Table S5

Table S5. The elemental analysis data of QAP.

Varied amine based QAP	N(wt.%)	C(wt.%)	H(wt.%)	O(wt.%)
Ethylenediamine	12.82	58.51	4.221	24.45
Propanediamine	9.562	62.63	4.731	23.08
Hexanediamine	6.949	65.45	6.107	21.49
o-Phenylenediamine	11.94	68.64	3.939	15.48
melamine	51.51	38.77	4.180	5.54

Table S6

Table S6. The Summary of the XPS C1s data of the ethylenediamine based QAP.

	Aromatic and aliphatic C		C–OH/C=N/C–N		C=O	
	Binding energy (eV)	At.%	Binding energy (eV)	At.%	Binding energy (eV)	At.%
Fresh	284.6	70.3	286.1	17.8	288.5	11.9
Used	284.6	49.8	285.7	38.0	288.3	12.2

Table S7

Table S7. The Summary of the XPS O1s data of the ethylenediamine based QAP.

	C=O		C–OH	
	Binding energy (eV)	At.%	Binding energy (eV)	At.%
Fresh	531.6	57.0	533.0	43.0
Used	531.6	73.1	533.3	26.9

Table S8

Table S8. The Summary of the XPS N1s data of the ethylenediamine based QAP.

	imine (–N=)		amine (–N–)	
	Binding energy (eV)	At.%	Binding energy (eV)	At.%
Fresh	398.4	16.0	399.2	79.3
Used	398.6	7.7	399.7	92.3

5. References

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