

Supporting Information

Heterogeneous solvent-metal-free aerobic Oxidation of alcohol under ambient condition catalyzed by TEMPO-functionalized porous poly(ionic liquid)s

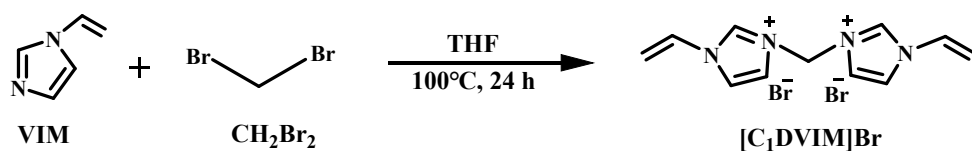
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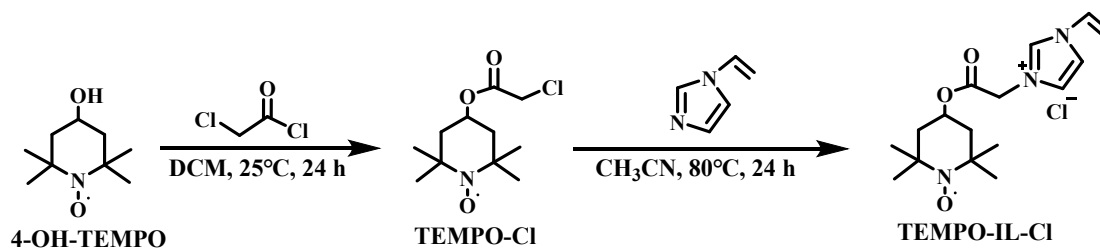
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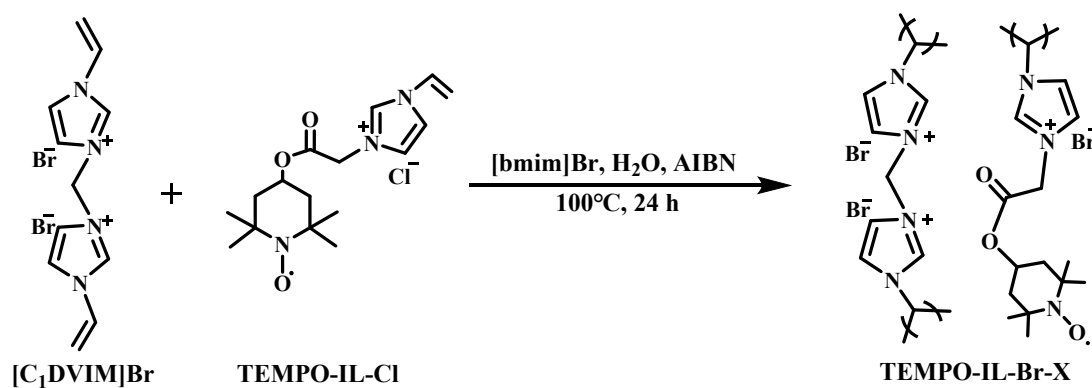
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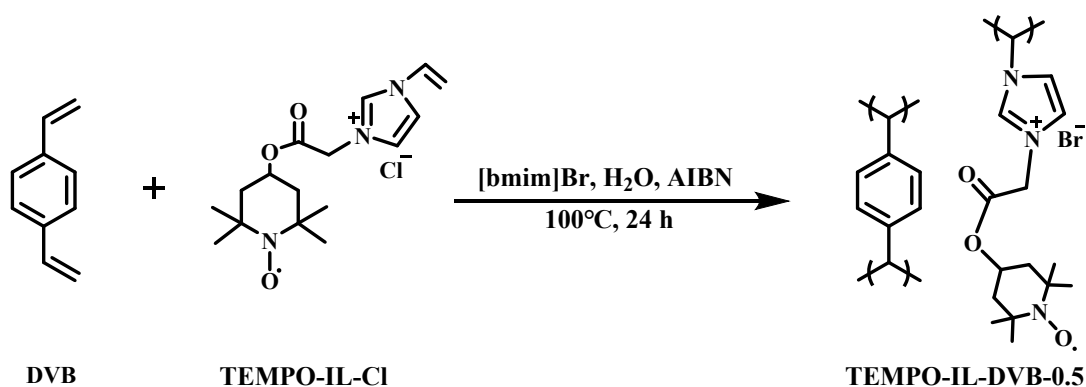
Scheme S1 Synthesis of rigid bis-vinylimidazolium salt monomer [C₁DVIM]⁺Br⁻.



Scheme S2 Synthesis of TEMPO functionalized ionic liquid monomer TEMPO-IL-Cl.



Scheme S3 Synthetic route of TEMPO-IL-Br-X. (X is the molar ratio of TEMPO-IL-Cl to [C₁DVIM]⁺Br⁻, X=1, 0.5, 0.2, 0.1)



Scheme S4 Synthetic route of TEMPO-IL-DVB-0.5.

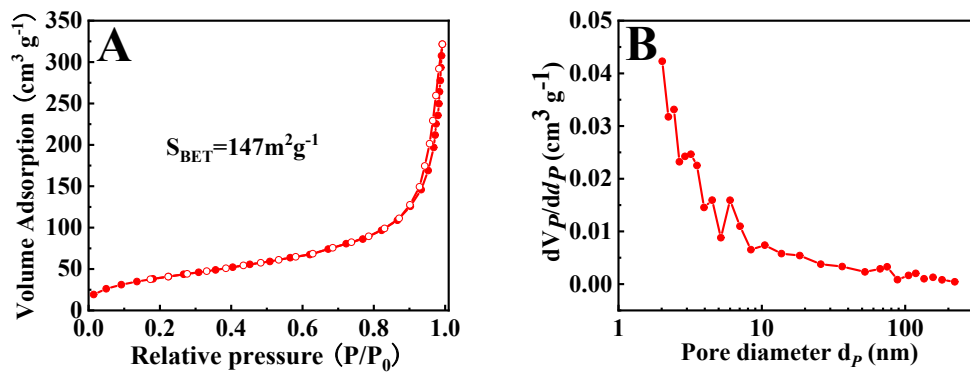


Fig. S1 (A) Nitrogen sorption isotherms and (B) pore size distribution curve of TEMPO-IL-DVB-0.5.

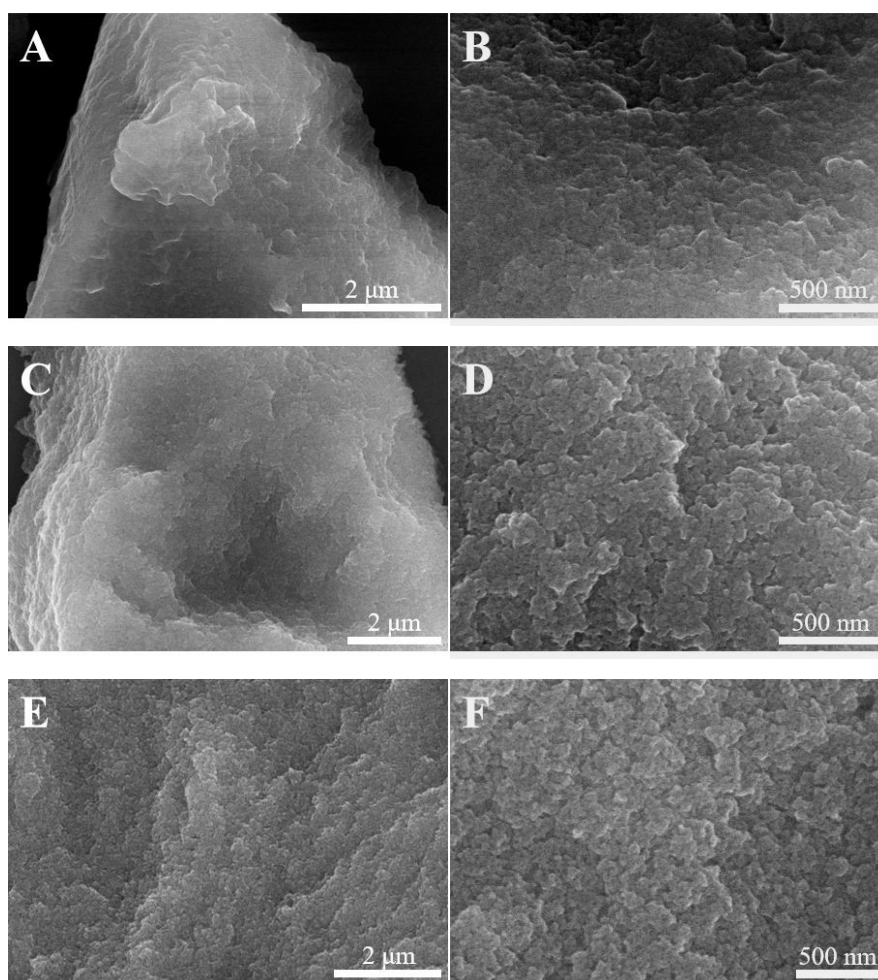


Fig. S2 SEM images of (A, B) TEMPO-IL-Br-1, (C, D) TEMPO-IL-Br-0.2, and (E, F) TEMPO-IL-Br-0.1.

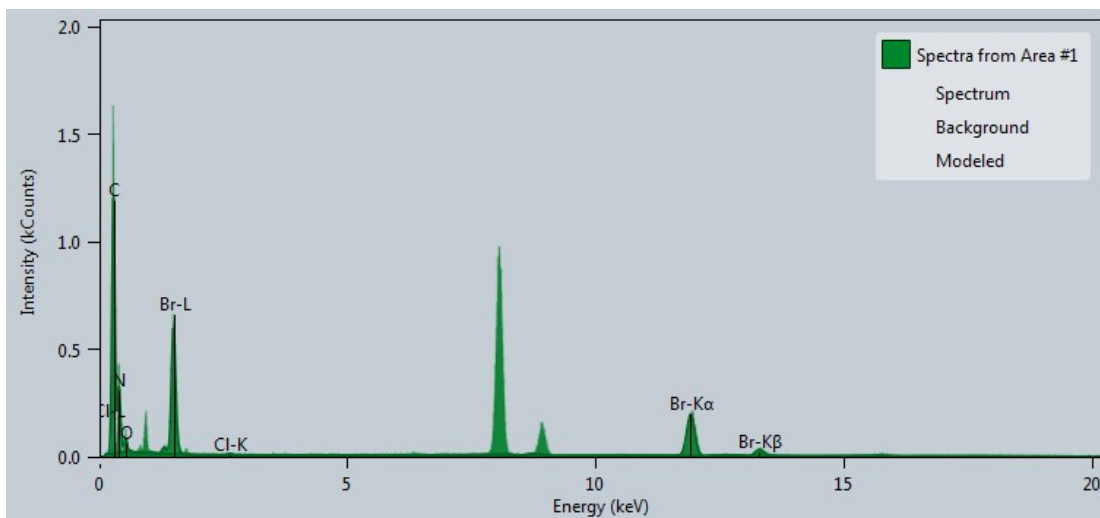


Fig. S3 EDS spectrum of TEMPO-IL-Br-0.5.

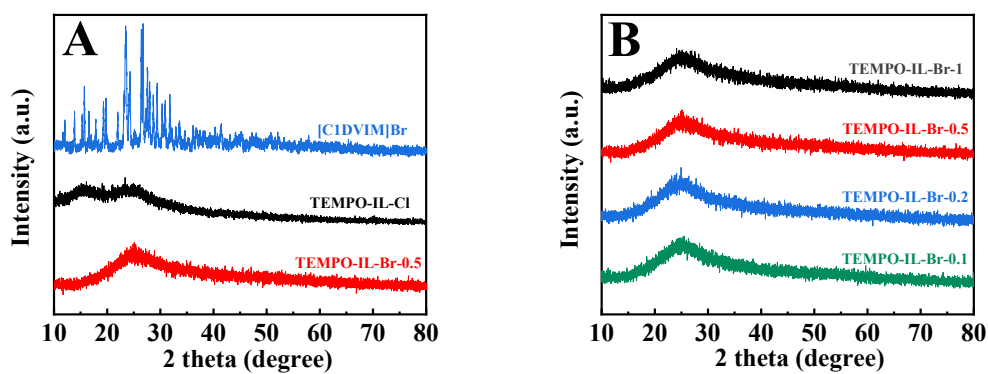


Fig. S4 XRD patterns of [C₁DVM]Br, TEMPO-IL-Cl and TEMPO-IL-Br-X (X=1, 0.5, 0.2, 0.1).

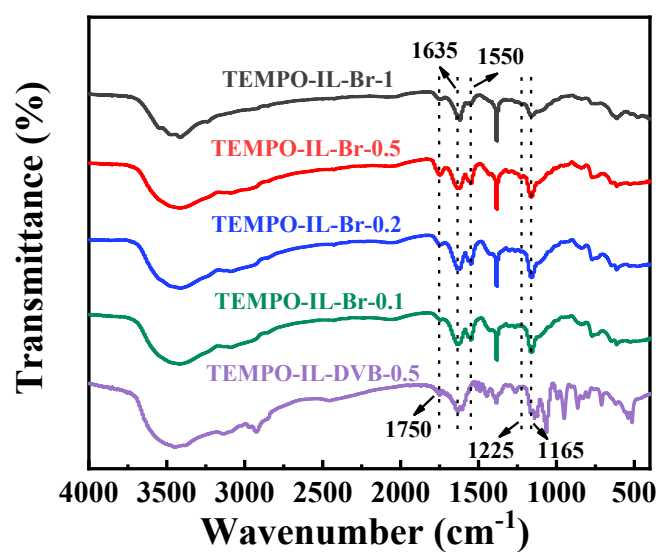


Fig. S5 FT-IR spectra of TEMPO-IL-Br-X (X=1, 0.5, 0.2, 0.1) and TEMPO-IL-DVB-0.5.

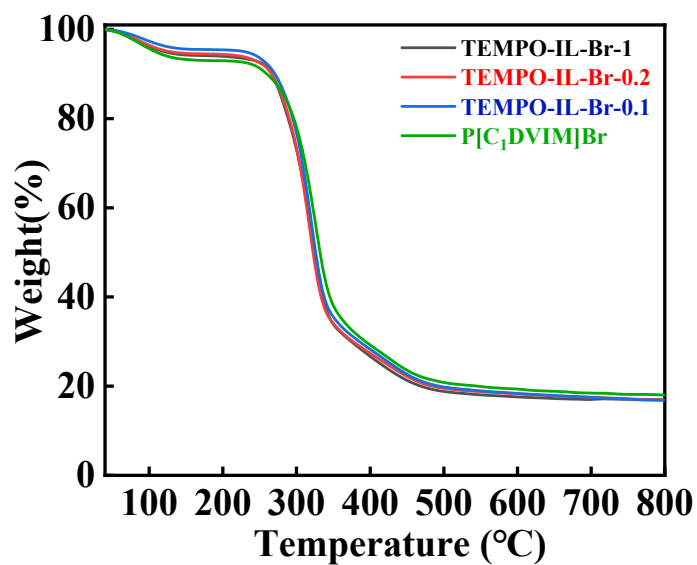


Fig. S6 Thermogravimetry curves of P[C₁DVIM]Br and TEMPO-IL-Br-X (X=1, 0.2, 0.1).

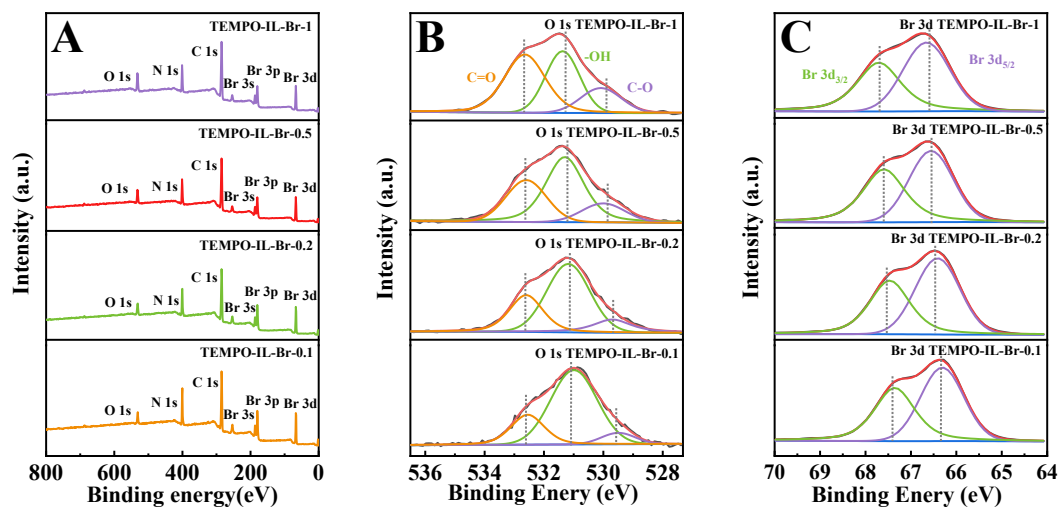


Fig. S7 (A) XPS survey scan spectra, (B) O 1s and (C) Br 3d XPS spectra of TEMPO-IL-Br-X (X=1,0.5,0.2,0.1).

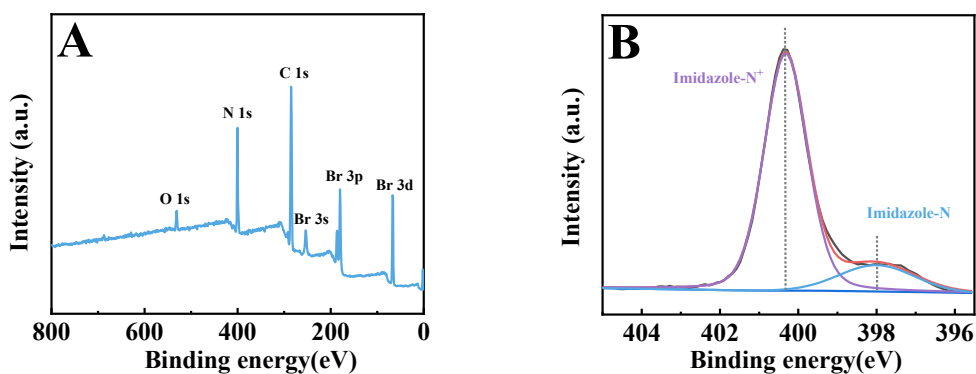


Fig. S8 (A) XPS survey scan spectrum and (B) N 1s XPS spectrum of P[C₁DVIM]Br.

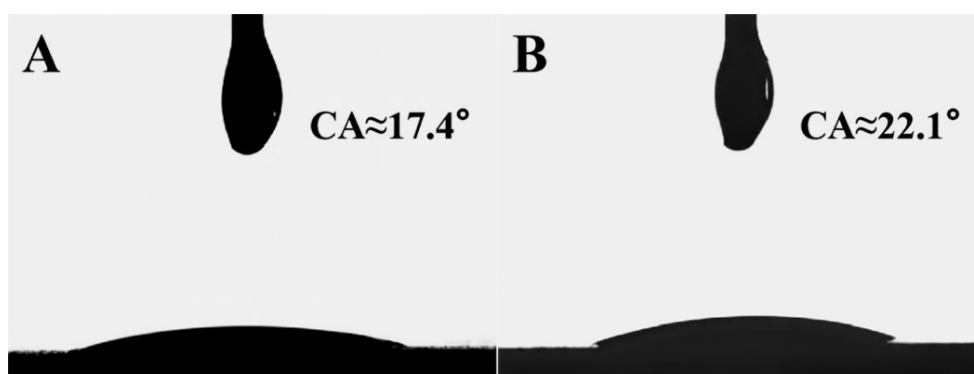


Fig. S9 Benzyl alcohol contact angle on a thin slice of (A) TEMPO-IL-Br-0.5 and (B) TEMPO-IL-DVB-0.5.

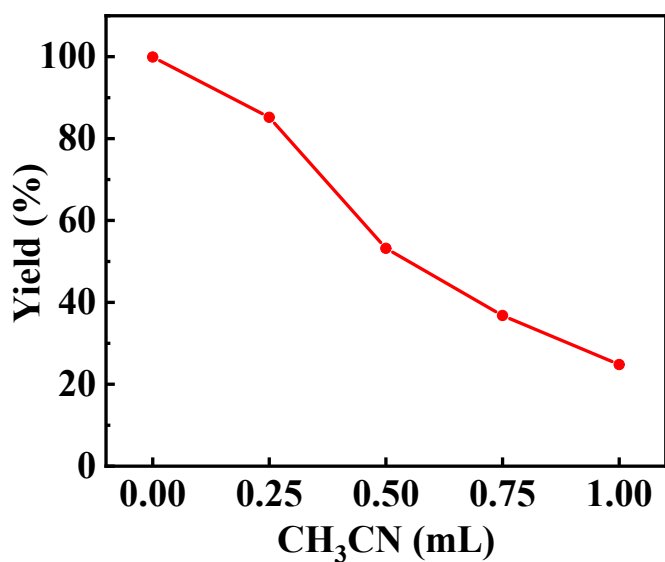


Fig. S10 Effect of CH₃CN dosage on the oxidation of benzyl alcohol.

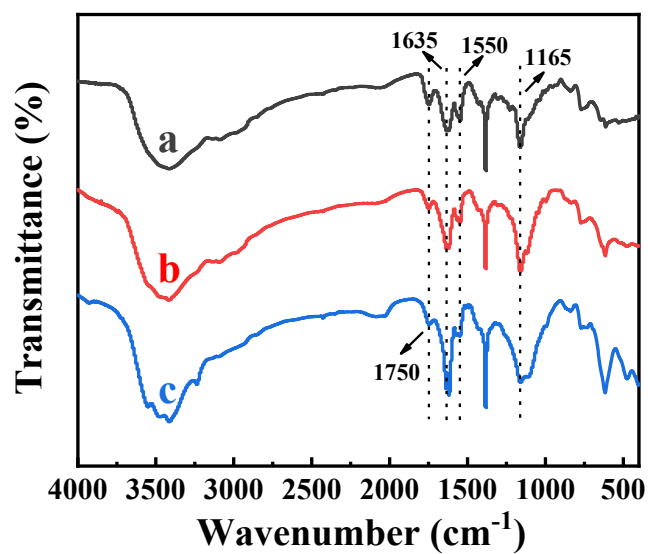


Fig. S11 FT-IR spectra of (a) fresh TEMPO-IL-Br-0.5, (b) recovered TEMPO-IL-Br-0.5 in CH₃CN and (c) recovered TEMPO-IL-Br-0.5 without solvent.

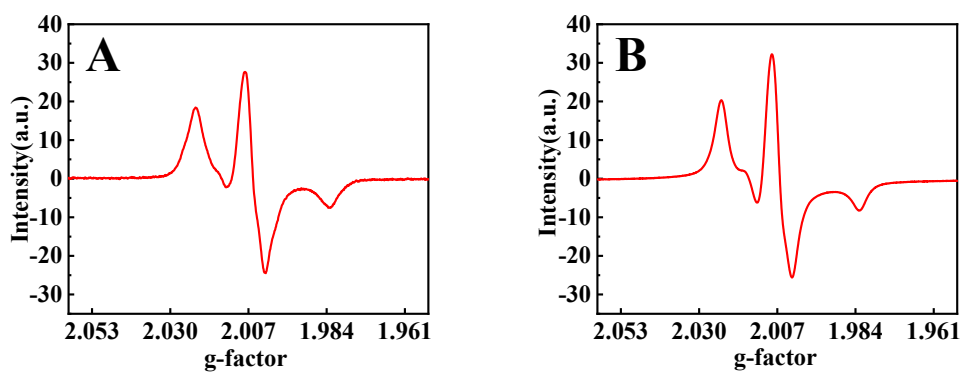


Fig. S12 Solid state EPR spectra of TEMPO-IL-Br-0.5 recovered in (A) solvent-free and (B) CH₃CN.

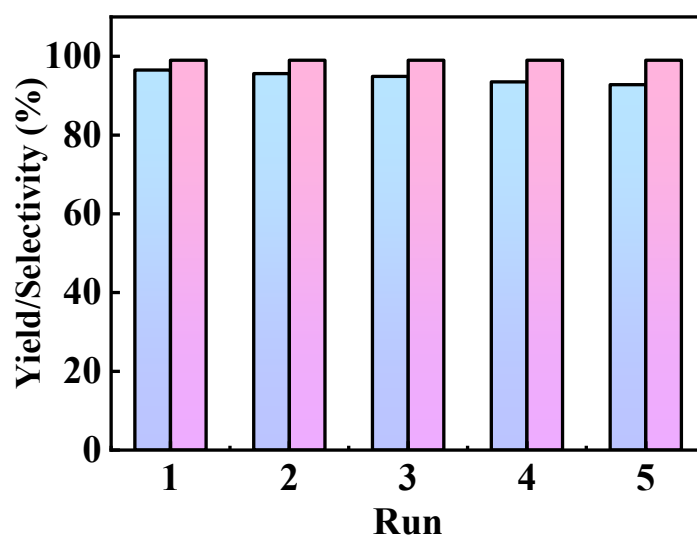


Fig. S13 Recyclability study of TEMPO-IL-Br-0.5 in CH₃CN for the oxidation of benzyl alcohol.

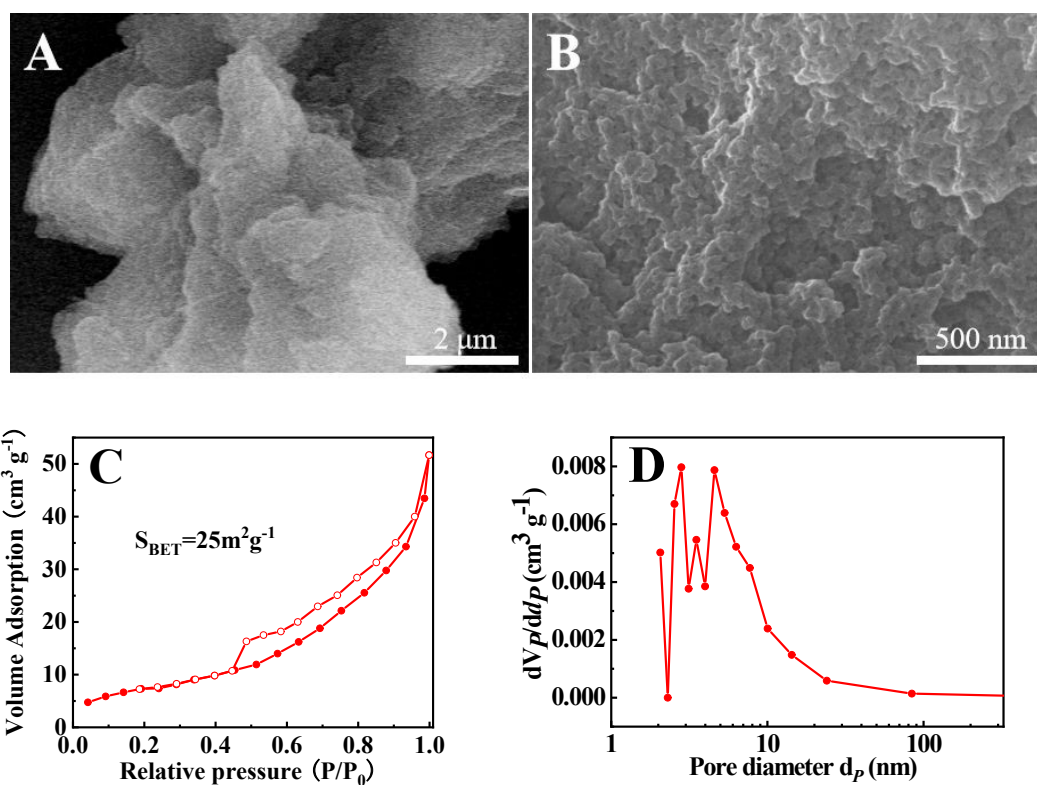
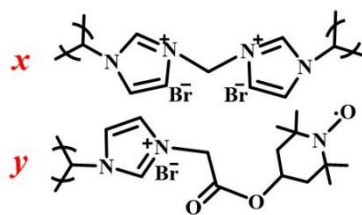


Fig. S14 (A, B) SEM images, (C) Nitrogen sorption isotherms and (D) pore size distribution curve of recovered TEMPO-IL-Br-0.5.

Table S1

The proportional relation of chemical component in the final copolymers.



Entry	Samples	x: y
1	TEMPO-IL-Br-1	1 : 1.147
2	TEMPO-IL-Br-0.5	1 : 0.736
3	TEMPO-IL-Br-0.2	1 : 0.479
4	TEMPO-IL-Br-0.1	1 : 0.250

Table S2

Elemental analysis data of different samples.

Entry	Samples	Nitrogen(%)	Carbon(%)	Hydrogen(%)
1	TEMPO-IL-Cl	11.11	51.34	7.36
2	[C ₁ DVIM]Br	15.53	36.85	3.99
3	TEMPO-IL-Br-1	12.92	38.83	5.08
4	TEMPO-IL-Br-0.5	13.43	37.95	5.32
5	TEMPO-IL-Br-0.2	13.9	35.85	5.21
6	TEMPO-IL-Br-0.1	14.49	35.97	5.21
7	TEMPO-IL-Br-r	13.63	37.48	5.57
8	TEMPO-IL-DVB-0.5	3.05	78.57	7.51

TEMPO loading of TEMPO-IL-DVB-0.5 based on CHN analysis:

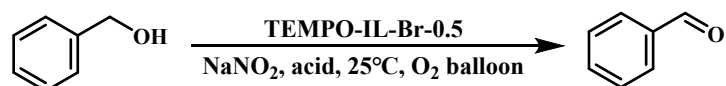
$$\frac{3.05\text{mg N}}{100\text{mg Sample}} \times \frac{1\text{mmol N}}{14\text{mg N}} \times \frac{1\text{mmol TEMPO}}{3\text{mmol N}} \times \frac{1000\text{mg Sample}}{1\text{g Sample}} = 0.726\text{mmol/g}$$

Table S3The aerobic oxidation of benzyl alcohol under various conditions.^a

Entry	Solvent(ml)	Con. ^b (%)	Sel. ^b (%)	Yield ^b (%)
1	MeOH	3.4	8.4	0.3
2	EtOH	8.2	40.0	3.3
3	H ₂ O	9.8	95.1	9.3
4	THF	42.1	98.6	41.5
5	EtOAc	58.6	73.9	43.3
6	Toluene	50.1	99.0	49.6
7	N-hexane	72.0	99.1	71.4
8	DCM	77.7	99.8	77.5
9	MeCN	85.2	99.9	85.1
10	none	99.9	99.9	99.9

^a Reaction conditions: 1.0 mmol of alcohol, 13.0 mg of TEMPO-IL-Br-0.5 (1.5 mol% of nitroxide radical), 5.5 mg of NaNO₂ (8.0 mol%), and 4.4 μL of H₂SO₄ (8.0 mol%) in 0.25 mL of solvent with an O₂ balloon at 25°C.

^b Determined by GC.

Table S4The aerobic oxidation of benzyl alcohol in the presence of different acid.^a

Entry	Acid (mol%)	Con. ^b (%)	Sel. ^b (%)
1	-	0	-
2	HOAc(8)	9.3	>99
3	HNO ₃ (8)	66.2	>99
4	HCl(8)	96.5	>99
5	H ₂ SO ₄ (8)	99.9	>99

^a Reaction conditions: 1.0 mmol of benzyl alcohol, 13.0 mg TEMPO-IL-Br-0.5(1.5 mol% of nitroxide radicals), 5.5 mg of NaNO₂ (8.0 mol%) with an O₂ balloon at 25°C for 5h.

^b The Conversion and selectivity were determined by GC.

Table S5Recovery performance of TEMPO-IL-Br-0.5 under solvent-free conditions.^a

Entry	TBAB (mol%)	Yield (%) ^c
1	0	30
2 ^b	6	91

^a Reaction conditions: 1 mmol of alcohol, 13.0 mg of TEMPO-IL-Br-0.5 (1.5 mol% of nitroxide radical), 5.5 mg of NaNO₂ (8.0 mol%), and 4.4 μL of H₂SO₄ (8.0 mol%) with an O₂ balloon at 25°C.

^b Reaction conditions: 0.5 mmol of alcohol, 9.7 mg TBAB (6%) and all other conditions remained the same.

^c Determined by GC.

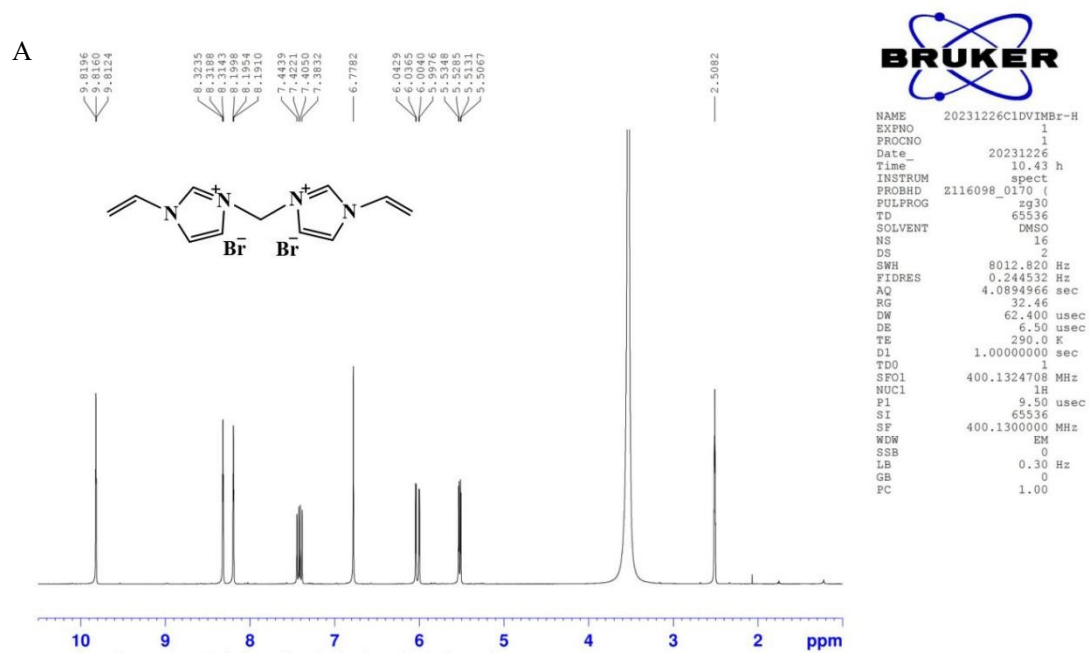
^d Wash with HAc, MeCN, and DCM for 0.5 h respectively.

Table S6

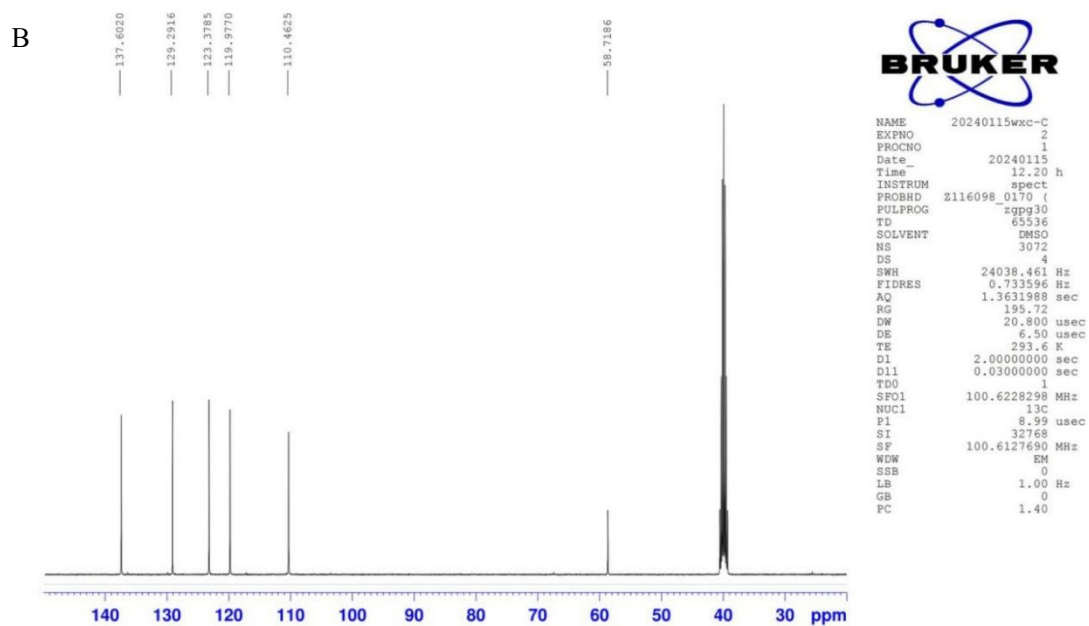
Comparison of catalysis performance for various TEMPO-anchored materials.

Entry	Catalyst (mol%)	Conditions	Solvent	Temp (°C)	Yield (%)	TOF ^a (h ⁻¹)	Ref.
1	TEMPO-IL-Br-0.5 (1.5)	NaNO ₂ , H ₂ SO ₄ , O ₂ , 5 h	-	25	>99	>13.3	This work
2	FRPCP (3.5)	TBN, O ₂ , 24 h	C ₂ D ₂ Cl ₄	80	94	1.1	1
3	PEG-TEMPO (5)	Mn(NO ₃) ₂ , Co(NO ₃) ₂ , O ₂ , 3 h	AcOH	25	>99	6.7	2
4	silica-supported TEMPO (20)	NO ⁺ BF ₄ ⁻ , O ₂ , 4 h	DCM	25	97	1.2	3
5	NMI-TEMPO-1 (5)	CuI, ^t Bu ₂ -bipy, air, 3 h	CH ₃ CN	25	96	6.4	4
6	UiO-67-TEMPO(38%) (1)	TBN, durene, O ₂ , 24 h	DCE	25	>99	4.2	5
7	UiO-68-TEMPO (5)	TBN, air, 8 h	DCE+H ₂ O	80	>99	2.5	6
8	iGO-TEMPO (1)	NaNO ₂ , O ₂ , 20 h	DCM+ACOH	25	>99	5	7
9	HPAF-TEMPO (5)	TBN, air, 6 h	PhCF ₃	80	96	3.3	8
10	IL/SMNP (50)	2 atm O ₂ , 5 h	toluene	80	97	0.4	9
11	PAES-TEMPO/NO _x (15.7)	air, 6 h	DCM	25	>99	1.1	10
12	MIL-101(Fe)/TEMPO-IsoNTA (5)	TBN, O ₂ , 1.5 h	PhCF ₃	80	>99	13.3	11
13	IL@SBA-15-TEMPO (1)	TBN, O ₂ , 3.5 h	AcOH	40	>99	28.6	12
14	MNS-TEG-IL-TEMPO (0.9)	TBN, HNO ₃ , O ₂ , 5 h	H ₂ O	50	>99	22.2	13
15	TEMPO@PMO-IL-Br (1.5)	TBN, ACOH, O ₂ , 1 h	toluene	50	>99	66.7	14
16	JUC-566 (5)	NaNO ₂ , DBDMH, O ₂ , 0.15 h	AcOH	25	>99	132	15
17	TEMPO-CMP-4 (5)	NaNO ₂ , DBDMH, O ₂ , 0.5 h	AcOH	25	>99	40	16

^a Turnover frequency: yield of Benzyl alcohol (mmol) per [TEMPO content (mmol) × reaction time (h)], We assume that all of the TEMPO sites participated in the reaction.



^1H NMR (400 MHz, DMSO- D_6) δ (ppm): 9.81 (t, 1H), 8.31(t, 1H), 8.19(t, 1H), 7.42(q, 1H), 6.77(s, 1H), 6.03(q, 1H), 5.52(q, 1H).



^{13}C NMR (100 MHz, DMSO- D_6) δ (ppm): 137.6, 129.3, 123.4, 120.0, 110.5, 58.7.

Fig. S15 (A) ^1H NMR and (B) ^{13}C NMR of $[\text{C}_1\text{DVIM}]\text{Br}$ using DMSO as the solvent.

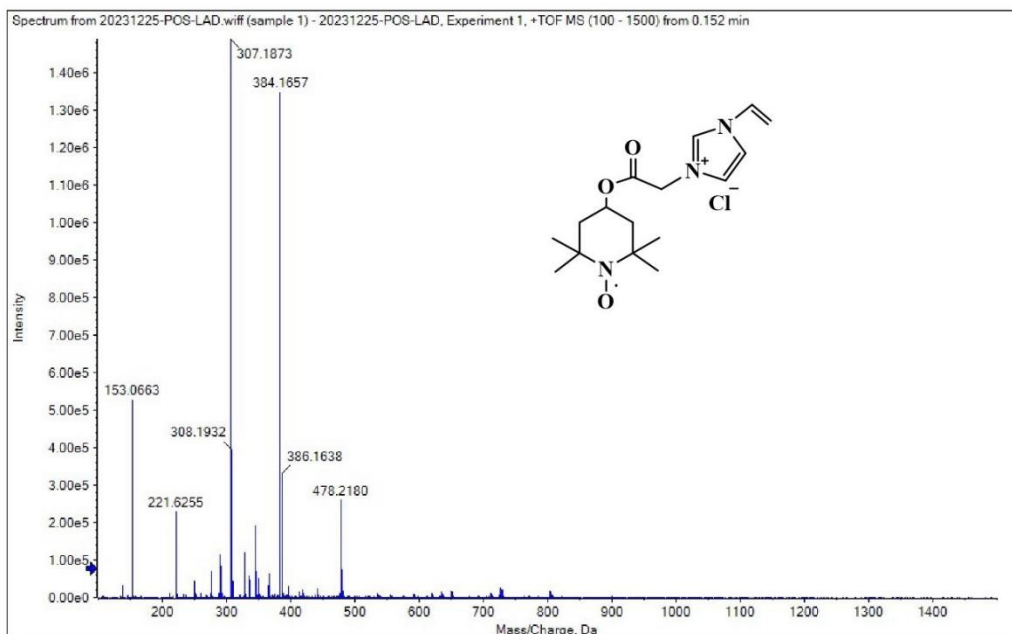
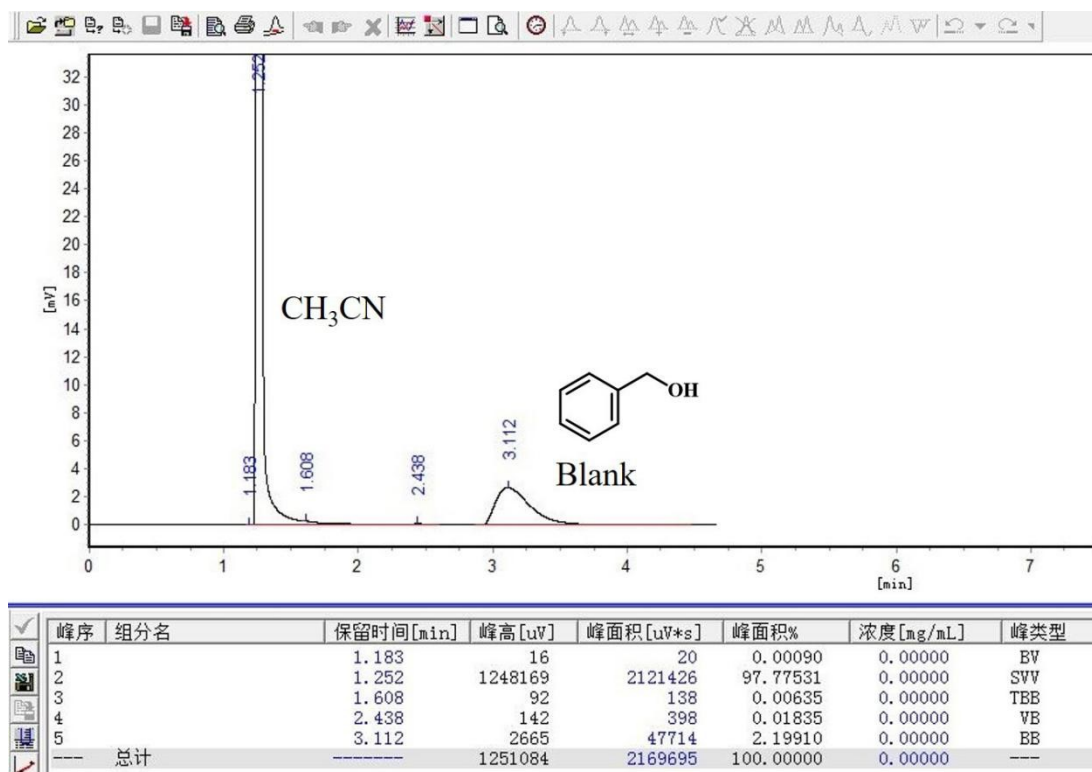
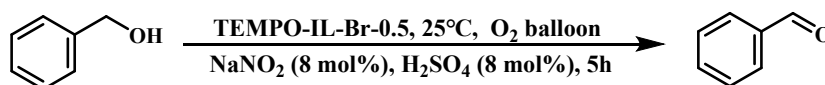
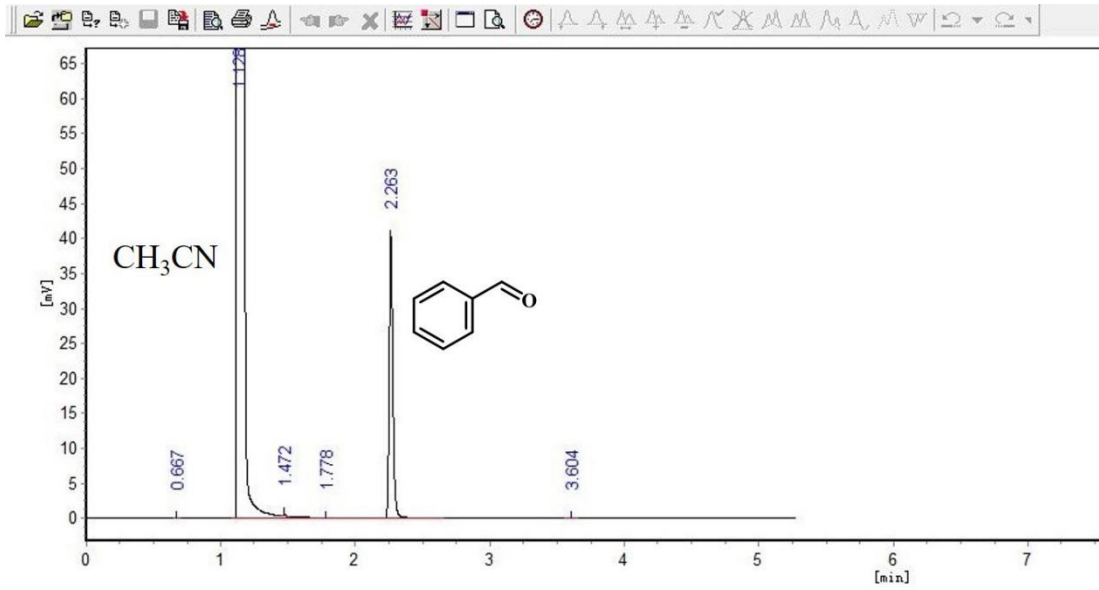


Fig. S16 MS spectrum of the TEMPO-IL-Cl, MALDI-TOF-MS: m/z : 307.1873, $[M-Cl]^+=307.39$, Calculated value: 342.84.

GC Chromatographs of the Reaction Products





峰序	组分名	保留时间[min]	峰高[uV]	峰面积[uV*s]	峰面积%	浓度[mg/mL]	峰类型
1		0.667	70	74	0.00316	0.00000	BB
2		1.128	1248147	2273036	96.73940	0.00000	SBV
3		1.472	169	214	0.00911	0.00000	TBB
4		1.778	12	15	0.00065	0.00000	TBB
5		2.263	40253	76265	3.24578	0.00000	VB
6		3.604	16	45	0.00190	0.00000	BB
总计			1288667	2349649	100.00000	0.00000	---

Supplementary References

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