SUPPLEMENTARY INFORMATION

Effective Electro-Oxidation of Hydroxymethylfurfural using Electrografted Immobilized Aminoxyl Radical

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4-amino-TEMPO synthesis.

A round-bottomed flask was charged with 1.0 g (6.4 mmol) of 2,2,6,6tetramethylpiperidine (compound 1, clear liquid) and 10 ml of ether (Et₂O). The solution was cooled to 0 °C and 1.08 ml (15.36 mmol) of acetic anhydride was added to the solution dropwise. Next, the mixture was allowed to warm to room temperature and left under stirring for 2 h, during which a white precipitate was produced. The solvent was removed, and the precipitate was washed with acetone and dried to obtain 2 g (7.75 mmol) of 2,2,5,5-tetramethylpiperidin-4acetamide acetate (compound 2), as shown in **Figure S1A**. Yield 75%. HRMS-ESI: calcd for $C_{11}H_{22}N_2O$ (M+H⁺) 199.1805, found 199.1831. ¹ Found in this work 199.1800.

In a 250 ml round-bottomed flask 500 mg (1.92 mmol) of Compound 2 was mixed with 20 ml of a 5% sodium carbonate aqueous solution. 79 mg (0.219 mmol) of EDTA-4Na⁺ and 79 mg (0.24 mmol) of sodium tungstate were further added before cooling the solution to 0-4 °C (ice bath). 1.58 ml (51.58 mmol) of cold 30% aqueous solution of hydrogen peroxide was slowly dropped into the clear solution; the mixture was then allowed to warm to room temperature and left or 72 h (**Figure S1B and C**). The orange suspension obtained was filtered off, and the filtrate was saturated with sodium carbonate. A new orange precipitate formed, which was filtered and dried to obtain 370 mg (1.73 mmol) of 1-oxyl-2,2,5,5-tetramethylpiperidin-4-acetamide as bright orange crystals, shown in **Figure S1D**. Yield 89.5%. HRMS (ESI): calcd for $C_{11}H_{22}N_2O_2$ (M+H⁺) 214.1676, found 214.1680.



Figure S1: Setup and products of 4-amino-TEMPO synthesis procedure part 1 of 2. **A**: Synthesized sample of 2,2,5,5-tetramethylpiperidin-4-acetamide acetate (compound 2). **B**: Photo of reaction vessel for synthesis of compound 3 with all reagents added, at initial reaction. **C**: Photo of reaction vessel for synthesis of compound 3 at the end of reaction. **D**: Synthesized sample of 1-oxyl-2,2,5,5-tetramethylpiperidin-4-acetamide (compound 3).

Synthesis of 1-oxyl-2,2,5,5-tetramethylpiperidin-4-amine (Compound 4).

200 mg of compound 3 was suspended into 12.5 ml of a 15% KOH aqueous solution, and the solution was heated to reflux (**Figure S2A**). After 36 h, the solution obtained was cooled to room temperature, saturated with K_2CO_3 , and extracted with Et_2O (**Figure S2B**). The organic phase was collected, dried (Na₂SO₄) and evaporated to obtain 147 mg (0.86 mmol) of compound 4 as a red liquid (1-oxyl-2,2,5,5-tetramethylpiperidin-4-amine) that crystallized at 14 °C (**Figure S2C**). This product is also known as 4-amino-TEMPO. Yield: 92.0 %. ¹HNMR (Acetone-d6, 300MHz) δ (ppm): from -15 to -35 (bm, 16H); IR (KBr): 2973 (vas TEMPOCH3), 2936 (vs TEMPOCH₃), 1459-1363 (δ TEMPOCH₃); HRMS (ESI): calcd for C₉H₂₀N₂O (M+H⁺) 172.1570, found 172.1578 ¹. Found in this work 172.1573.



Figure S2: Setup and products of 4-amino-TEMPO synthesis procedure part 2 of 2. **A**: Compound 3 in 15% KOH solution heated to reflux. **B**: 1-oxyl-2,2,5,5-tetramethylpiperidin-4-amine (4-amino-TEMPO) after liquid-liquid extraction. **C**: Sample of 4-amino-TEMPO after evaporation of solvent.

Synthesis characterization.



Figure S3: ESI-MS analysis report of 2,2,5,5-tetramethylpiperidin-4-acetamide acetate.



Figure S4: ¹H NMR spectrum of 1-oxyl-2,2,5,5-tetramethylpiperidin-4-acetamide. Using Bruker 500 MHz NMR, DMSO- d_6 standard.



Figure S5: ¹H NMR of 5-amino-TEMPOH, using Bruker 500 MHz NMR, DMSO-d₆ standard. Note that this sample was electrochemically reduced to the oxime form in order to avoid radical group's effect of masking NMR peaks.



Figure S6: 1-oxyl-2,2,5,5-tetramethylpiperidin-4-amine (4-amino-TEMPO).



HPLC Peak Assignment

Figure S7: Sample HPLC spectra of the HMFOR products, diluted 1:9 in 0.1 M KOH. Peak assignments determined from purchased standards.

Immobilization.

NaNO₂ disassociates with HCl to form the equivalent of disassociated nitrous acid HNO₂, which is the conjugate acid of nitrites. When amine is treated with HNO₂ under acidic conditions, the nitrosonium ions formed convert amine into diazonium ions. In typical Sandmeyer reaction, a halide salt (i.e., cuprous chloride) is used along with other catalysts to replace the diazonium, but in this electrochemical environment, it is hypothesized that the carbon atom instead forms a bond with carbon atoms on the electrode surface.² However, the precise mechanism is unknown at this time and is not central to the discussion.

Experimentally, this reaction is achieved through the following method adopted from literature ²: polished glassy carbon electrode or graphite electrode was submerged in 0.5 M HCl solution containing 5 mM NaNO₂ and previously synthesized 4-amino-TEMPO.



EIS model parameters.

Figure S8: EIS spectra of 3 mm diameter glassy carbon electrode at various number of electrografting cycles (20 mVs⁻¹), in an electrolyte of 0.2 M potassium nitrate and 2.5 mM potassium hexacyanoferrate probe.

Element	Parameter	Value	Estimated error (%)
R _s	R	41.535	0.86
R _P	R	719.57	1.254
CDE	Y ₀	4.3085 E-06	4.643
CFE	Ν	0.89223	1.193
14/	Y ₀	0.00052791	1.193
W	χ^2	0.051682	

Table S1: Glassy carbon electrode EIS fitting parameters.

Table S2: Electrografted 1 scan EIS fitting parameters.

Element	Parameter	Value	Estimated error (%)
R _s	R	41.372	1.468
R _P	R	3216.8	1.289
CDE	Y ₀	1.879 E-06	4.355
CPE	Ν	0.88836	0.58
14/	Y ₀	0.00050297	3.603
W	χ^2	0.11676	

Table S3: Electrografted 2 scans EIS fitting parameters.

Element	Parameter	Value	Estimated error (%)
R _s	R	42.653	0.816
R _P	R	1657.7	0.748
CDE	Y ₀	1.4664 E-06	3.073
CPE	Ν	0.91014	0.383
14/	Y ₀	0.00051825	1.669
W	χ^2	0.033951	

Table S4: Electrografted 3 scans EIS fitting parameters.

Element	Parameter	Value	Estimated error (%)
R _s	R	74.617	0.837

R _P	R	1795.5	0.859
CDE	Y ₀	1.5721E-06	3.740
CPE	Ν	0.89632	0.491
14/	Y ₀	0.00051991	1.996
vv	χ^2	0.041637	

Table S5: Electrografted 4 scans EIS fitting parameters.

Element	Parameter	Value	Estimated error (%)
R _s	R	40.195	1.322
R _P	R	2134.4	1.158
CDE	Y ₀	1.594 E-06	4.368
CPE	Ν	0.89254	0.556
	Y ₀	0.0004973	2.986
V	χ^2	0.082077	

Table S6: Electrografted 15 scans EIS fitting parameters.

Element	Parameter	Value	Estimated error (%)
R _s	R	109.16	0.985
R _P	R	3488.7	1.017
CDE	Y ₀	1.3709 E-06	3.994
CPE	Ν	0.88811	0.549
14/	Y ₀	0.00046148	3.513
W	χ^2	0.062106	

XPS results.

Table S7: XPS	N1s scan	results.
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Assignment	Peak found (eV)	Lit. peak (eV)	FWHM (eV)	Area (P) CPS (eV)	Atomic %
N1s Nitro-	406.78	405.7	1.64	2031.9	34.67
N1s amine	400.38	399.4	3.31	3846.37	65.33

Table S8: Elemental analysis of graphite electrografted with TEMPO.

Name	Peak (eV)	FWHM (eV)	Area (P) CPS (eV)	Atomic %
N1s	400.08	3.6	19848.92	0.9
C1s	284.39	1.68	1297633.5	87.9
01s	532.32	2.99	400636.28	11.2

Table S9: Elemental analysis of bare graphite.

Name	Peak (eV)	FWHM (eV)	Area (P) CPS (eV)	Atomic %
C1s	284.48	1.47	1589573.55	96.0
01s	532.3	3.37	161165.91	4.0

Table S10: Charge densities of N, O, C atoms in homogeneous and immobilized TEMPO radical.

Atom	Immobilized (electron)	Homogeneous (electron)
Ν	5.281	5.303
С	4.055	3.982
0	6.502	6.490

Table S11: Charge densities of N, O, C atoms in homogeneous and immobilized TEMPO-H.

Atom	Immobilized (electron)	Homogeneous (electron)
Ν	5.515	5.521
С	4.012	4.026

0	6.786	6.769

References

- 1.
- Y. Lu and S. Yamago, *Angewandte Chemie International Edition*, 2019, **58**, 3952-3956. M. Abdinejad, I. Santos Da Silva and H. B. Kraatz, *Journal of Materials Chemistry A*, 2. 2021, **9**, 9791-9797.