

**Electronic supplementary information**

**Metal-free electrocatalytic upcycling of polyethylene terephthalate plastic to C<sub>2</sub> products**

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## Experimental section

### Materials and methods

All the chemical reagents were purchased from commercial sources and used as received. Ethylene glycol (EG) was obtained from Alfa Aesar Pvt. Ltd. Potassium hydroxide (KOH) and D<sub>2</sub>O were purchased from Sigma. PET sheet was obtained from Akshay Polyfab Pvt. Ltd. Carbon cloth was purchased from Eliteck. Deionized water (18.2 MΩ cm resistivity at 25 °C, purified using a Millipore system) was used as the solvent for all the reported electrochemical experiments.

### Electrochemical Measurements

All the measurements were performed in a three-electrode system using a CHI440E potentiostat. Ag/AgCl (saturated KCl) and a Pt wire were used as the reference and counter electrodes, respectively. For bulk electrolysis of PET hydrolysate, 1X1 cm<sup>2</sup> carbon cloth and graphite rod were used as working and counter electrodes, respectively. All the potentials were converted to the normal hydrogen electrode (NHE) scale.

$$E_{\text{NHE}} (\text{V}) = E_{\text{Ag/AgCl}} + 0.197 \quad (\text{Equation S1})$$

or to a reversible hydrogen electrode (RHE) scale using the Nernst equation at room temperature:

$$E_{\text{RHE}} (\text{V}) = E_{\text{Ag/AgCl}} + 0.0592 \times \text{pH} + 0.197 \quad (\text{Equation S2})$$

$$\% \text{ Formate selectivity} = \frac{\text{Moles of formate produced}/2}{\text{Mole of converted EG}} \times 100$$

$$\% \text{ FY}_{\text{Formate}} = \frac{\text{Moles of formate produced} \times 96485 \text{ C mol}^{-1} \times 3}{\text{Mole of converted EG}} \times 100$$

$$\% \text{ Glycolate selectivity} = \frac{\text{Moles of produced glycolate}/2}{\text{Mole of converted EG}} \times 100$$

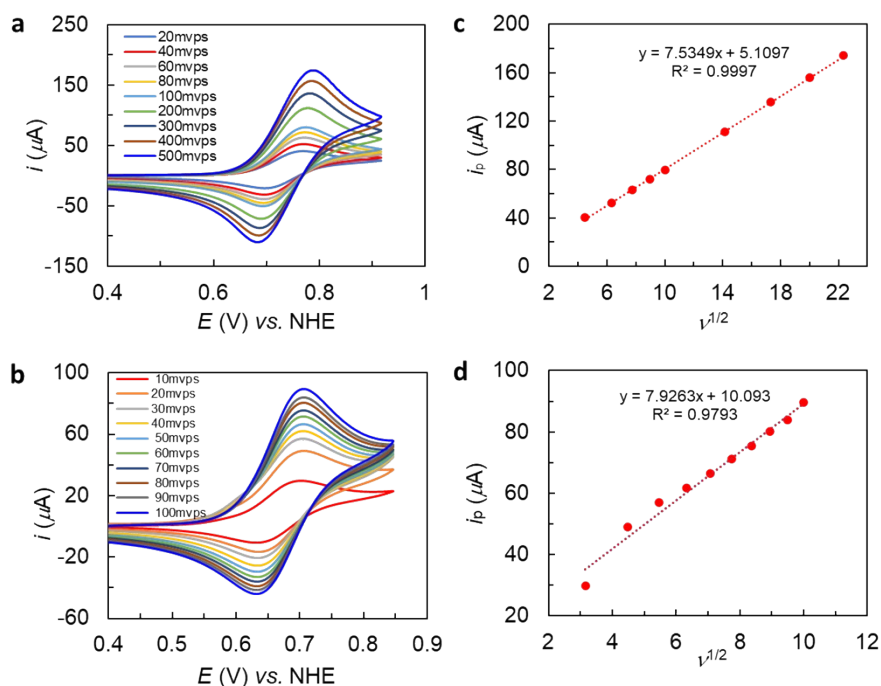
$$\% \text{ FY}_{\text{Glycolate}} = \frac{\text{Moles of glycolate produced} \times 96485 \text{ C mol}^{-1} \times 4}{\text{Mole of converted EG}} \times 100$$

### Product Analysis

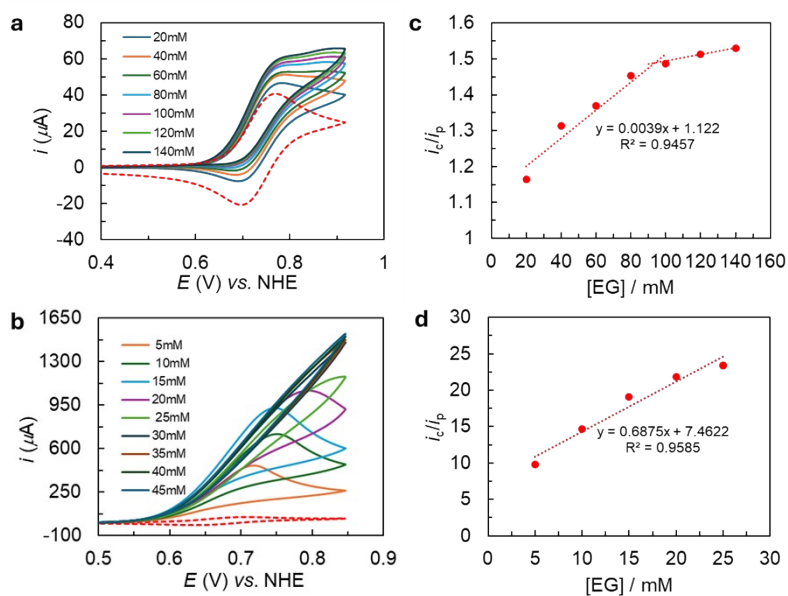
The product yields for post-electrolysis solutions were obtained through NMR (Bruker Avance III, 500 MHz) having 1,4-dioxane (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) as an internal standard in D<sub>2</sub>O. Hydrogen evolution measurements: The amount of produced hydrogen in the reactor headspace was analyzed using a gas chromatograph (CIC-Dhruva) equipped with a thermal conductivity detector (TCD). Oxalate and carbonate quantification cannot be precisely done due to a lack of instrumental facility. However, a <sup>13</sup>C-NMR quantification method was used.<sup>1</sup> The parameters for the <sup>13</sup>C-NMR are: pulse width = 8.9 μs, relaxation delay = 2s, AQ = 1.10s.

**Table S1.** Electrocatalysts reported for PET or Ethylene glycol (EG) oxidation to glycolate.

| Entry | Catalyst  | Substrate            | <i>E</i> (V<br>vs.<br>RHE) | Condition | Product | FY                   | Separation<br>Technique                           | Quantification<br>Technique | Ref.         |
|-------|---|----------------------|----------------------------|-----------|---------|----------------------|---|-----------------------------|--------------|
| 1     | Pt/ $\gamma$ -NiOOH/NF                              | PET derived EG       | 0.55 V                     | 1M KOH    | GA      | 97%                  | Electrolyte evaporation, liquid-liquid extraction | NMR and HPLC                | 2            |
| 2     | Pd <sub>1</sub> Ag <sub>1</sub> alloy nanoparticles | PET derived EG       | 0.75 V                     | 1M KOH    | GA      | 97% (GA selectivity) | Electrolyte evaporation, recrystallization        | NMR                         | 3            |
| 3     | Pd Ni(OH) <sub>2</sub>                              | PET derived EG       | 1.15 V                     | 1M KOH    | GA      | >85%                 | Electrolyte evaporation, recrystallization        | NMR                         | 4            |
| 4     | Pt-Ni(OH) <sub>2</sub> /NF                          | PET derived EG       | 0.69 V                     | 1M KOH    | GA      | 93%                  | Electrolyte evaporation, recrystallization        | NMR and HPLC                | 5            |
| 5     | PdAg/NF   | EG                   | 1 V                        | 0.5M KOH  | GA      | 92%                  | -   | NMR                         | 6            |
| 6     | PdN <sub>4</sub> /CuN <sub>4</sub>                  | EG                   | 1.0 V                      | 1M NaOH   | GA      | >80%                 | -   | NMR                         | 7            |
| 7     | Pd-PdSe Nanosheets                                  | EG                   | 0.76 V                     | 1M KOH    | GA      |                      |   | HPLC                        | 8            |
| 8     | Co  | EG                   | 1.60 V                     | 1M NaOH   | GA      | 43%                  | -   | HPLC                        | 9            |
| 9     | Au/Ni(OH) <sub>2</sub>                              | PET derived EG       | 1.15V                      | 3M KOH    | GA      | 96%                  | Neutralization and precipitation                  | HPLC                        | 10           |
| 10    | TEMPO   | EG<br>PET derived EG | 1.5V                       | 1M KOH    | GA      | 44%                  | -   | NMR                         | Current Work |

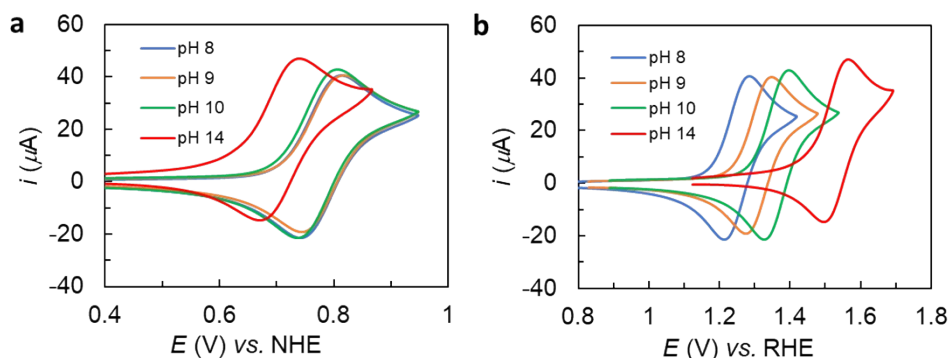


**Figure S1.** Left panel: Scan rate dependence CV for TEMPO at (a) pH 10 and (b) at pH 14; Right panel: Plot of  $i_p$  vs.  $v^{1/2}$  showing a linear fit suggesting the redox process is diffusion controlled at (c) pH 10 and (d) pH 14. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; the potential is adjusted to the NHE scale.

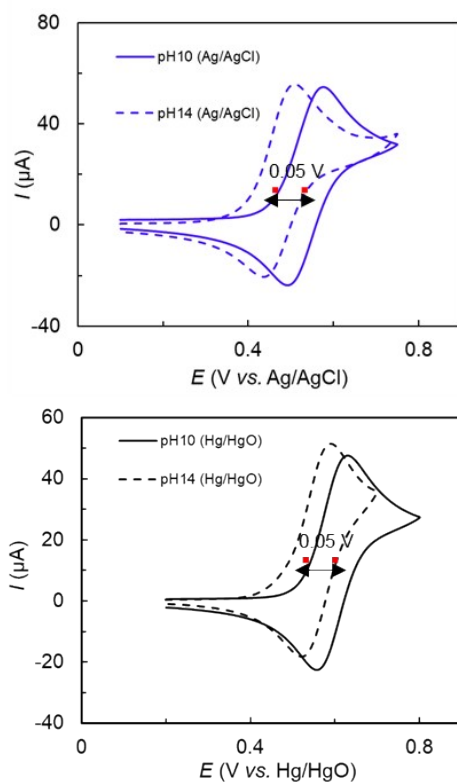


**Figure S2.** Left panel: Cyclic voltammogram of EGOR with varying concentrations of EG at (a) pH 10 and (b) at pH 14 in the presence of 5 mM TEMPO. The Red dashed line represents the cyclic voltammogram of 5mM TEMPO; right panel: Plot of corresponding  $i_c/i_p$  vs. [EG] at (c) pH 10 and (d) at pH 14; suggesting the catalysis is first order with respect to the EG concentration at both the pHs. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; the potential is adjusted to the NHE scale. Scan rate 20mV/s.

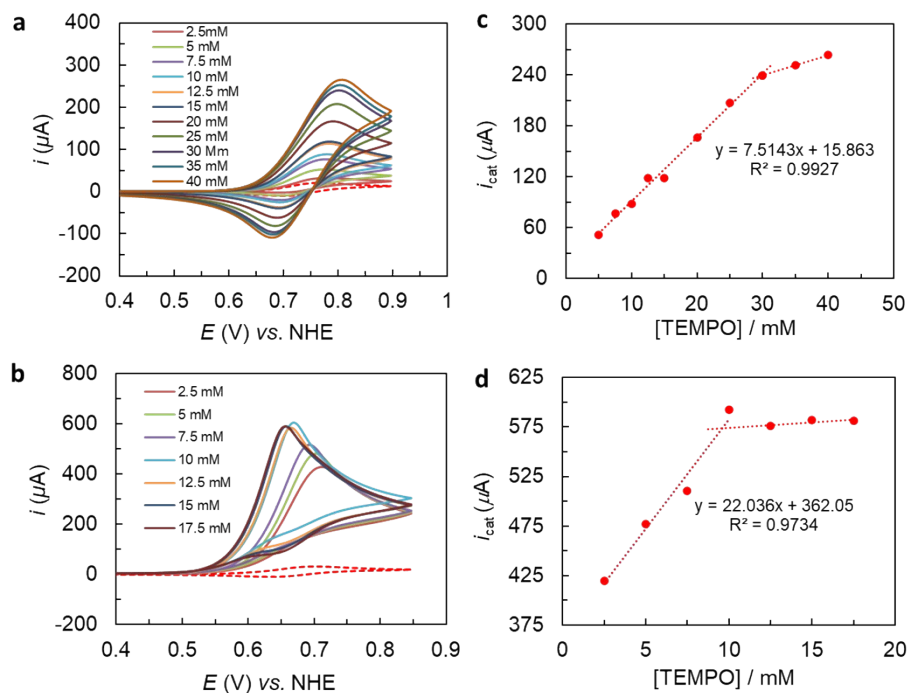
Beyond 30 mM, there is practically no change in the catalytic current, and the peak shape of the catalytic wave is also missing. The current at 0.8 V is considered to be the  $i_c$  for the plot d.



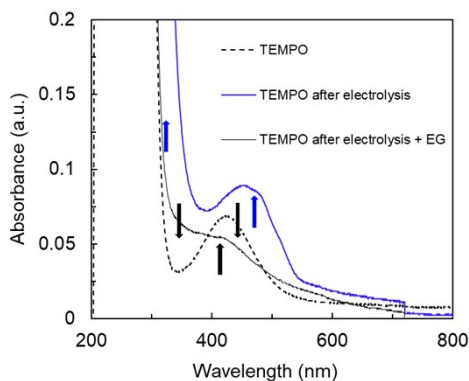
**Figure S3.** pH dependence CV of the process  $\text{TEMPO} \rightleftharpoons \text{TEMPO}^+$  (a) in NHE scale and (b) in RHE scale. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; the potential is adjusted to the NHE scale. Scan rate 20mV/s.



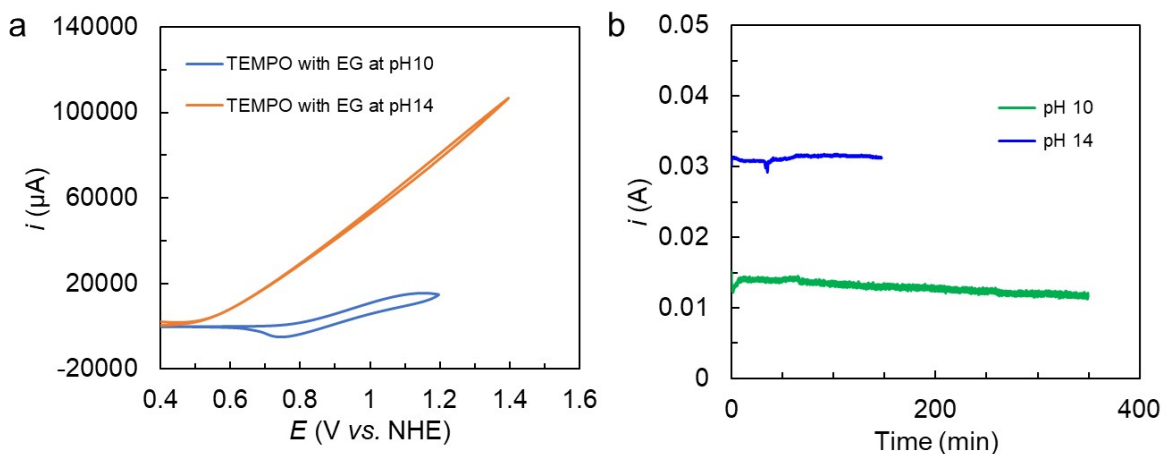
**Figure S4.** CV of TEMPO at pH 14 and pH 10 with different reference electrodes.



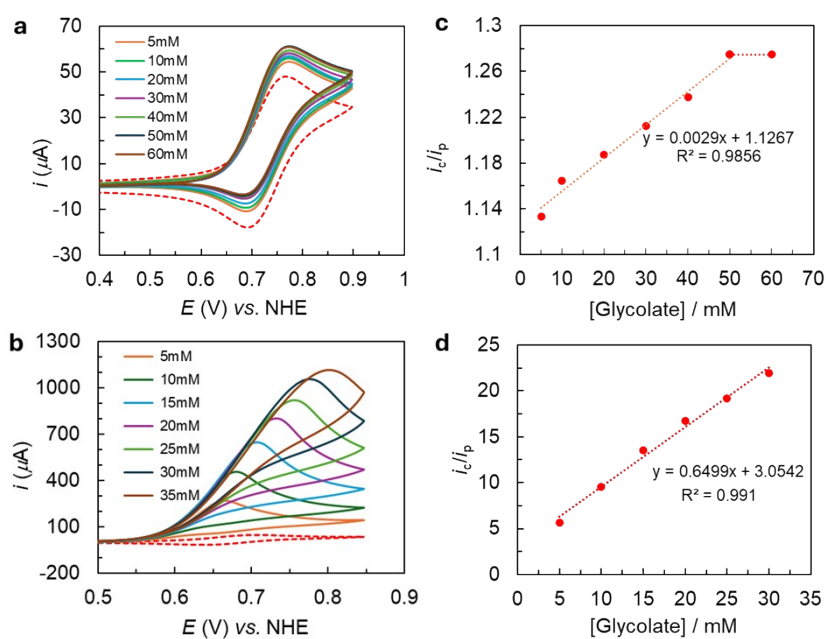
**Figure S5.** Left panel: Cyclic voltammogram of EGOR with varying concentrations of TEMPO at (a) pH 10 and (b) at pH 14 in the presence of 5mM EG. The Red dashed line represents the cyclic voltammogram of 2.5mM TEMPO; right panel: Plot of corresponding  $i_c/i_p$  vs. [TEMPO] at (c) pH 10 and (d) at pH 14; suggesting the catalysis is first order with respect to the TEMPO concentration at both the pHs. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; the potential is adjusted to the NHE scale. Scan rate 20mV/s.



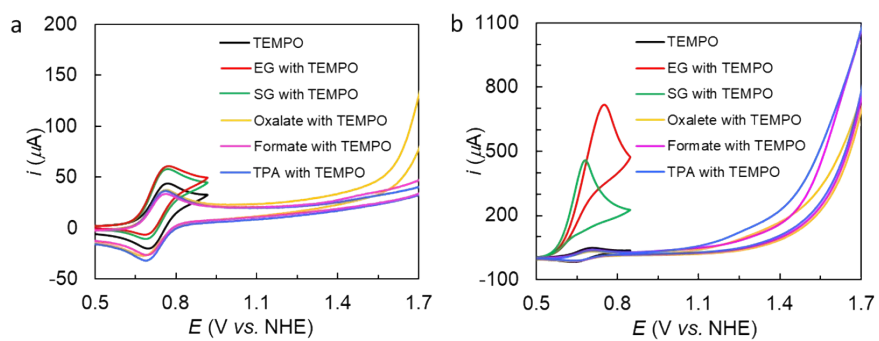
**Figure S6.** UV-Vis of the 5 mM of TEMPO (black dashed line), TEMPO after electro-oxidation at  $\sim 0.9$  V to form TEMPO-oxoammonium (blue line) and after the addition of 50 mM EG (black line) at pH 10 with carbon cloth as the working electrode.



**Figure S7.** (a) Cyclic voltammogram of TEMPO-mediated EGOR at pH 10 and pH 14 with carbon cloth as a working electrode; and (b) the corresponding  $i$  vs.  $t$  curve for the electrolysis at constant potential related to Figure 2a.

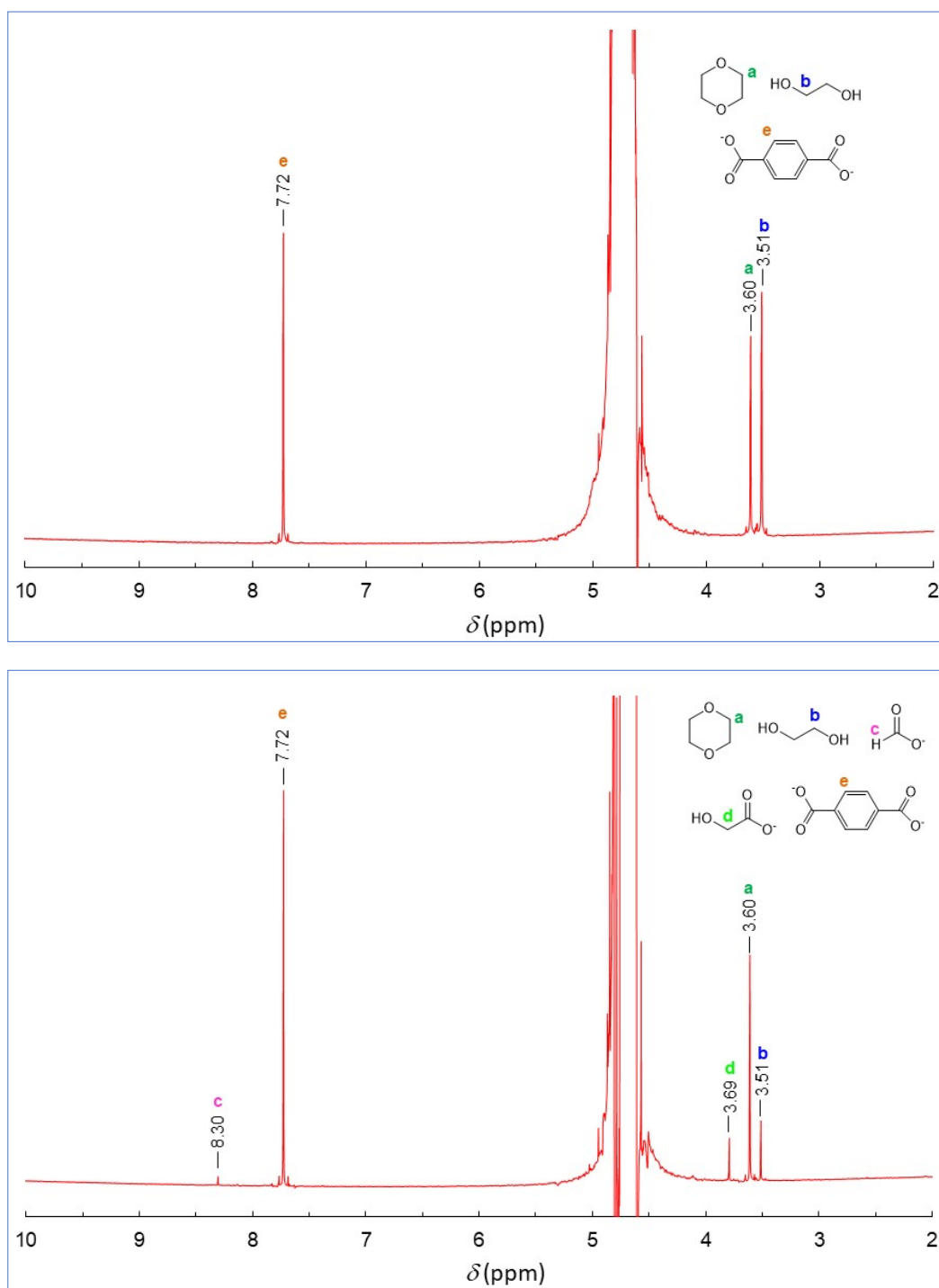


**Figure S8.** Left panel: Cyclic voltammogram of SGOR with varying concentrations of SG at (a) pH 10 and (b) at pH 14 in the presence of 5 mM TEMPO. The Red dashed line represents the cyclic voltammogram of 5mM TEMPO; right panel: Plot of corresponding  $i_c/i_p$  vs. [SG] at (c) pH 10 and (d) at pH 14; suggesting the catalysis is first order with respect to the SG concentration at both the pHs. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; the potential is adjusted to the NHE scale. Scan rate 20mV/s.

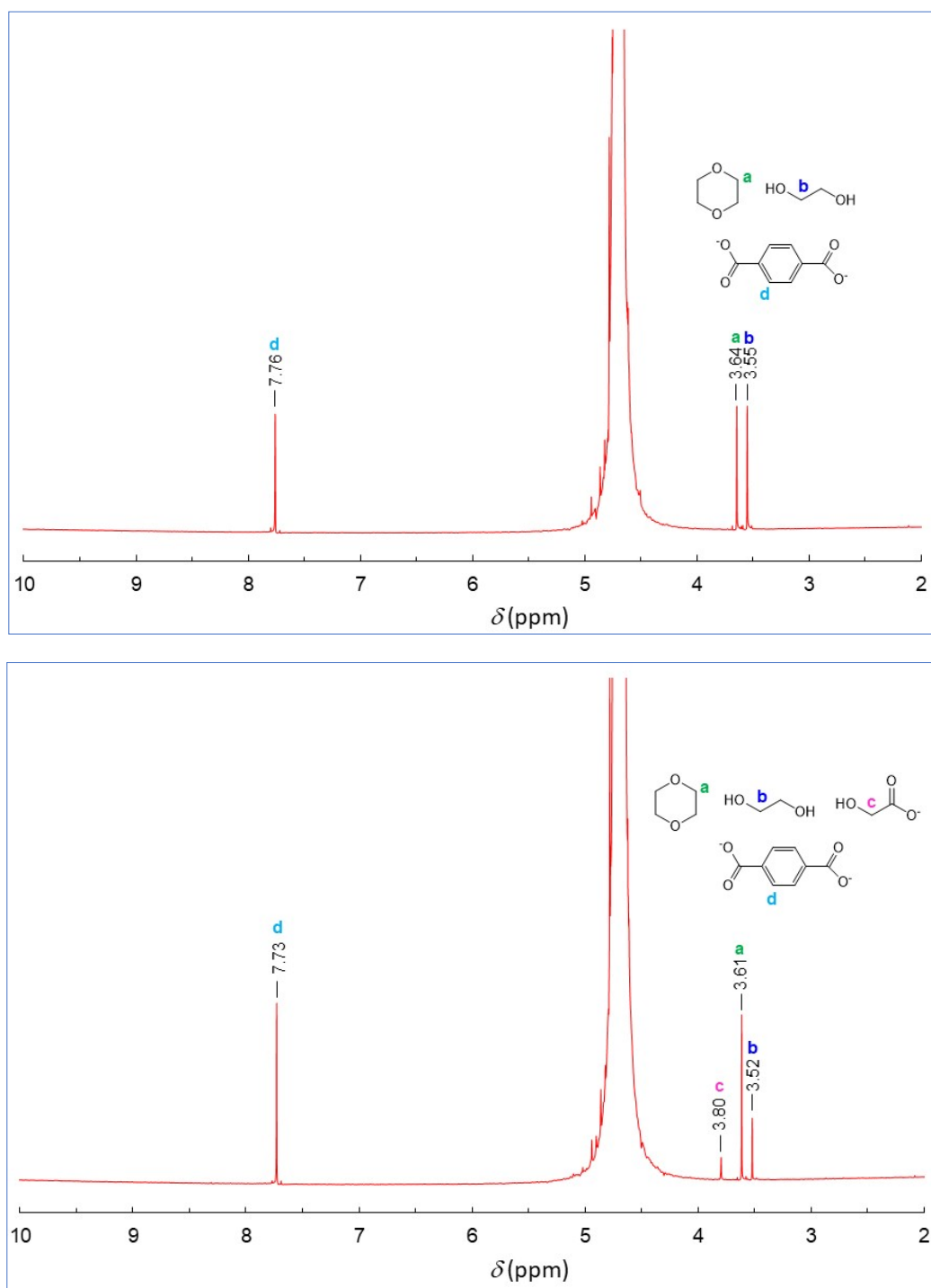


**Figure S9.** Cyclic voltammograms of 10mM of EG, SG, Oxalate, Formate, and TPA in the presence of 5mM TEMPO at (a) pH 10 and (b) pH 14. Experimental conditions: glassy carbon, Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively; the potential is adjusted to the NHE scale. Scan rate 20mV/s.

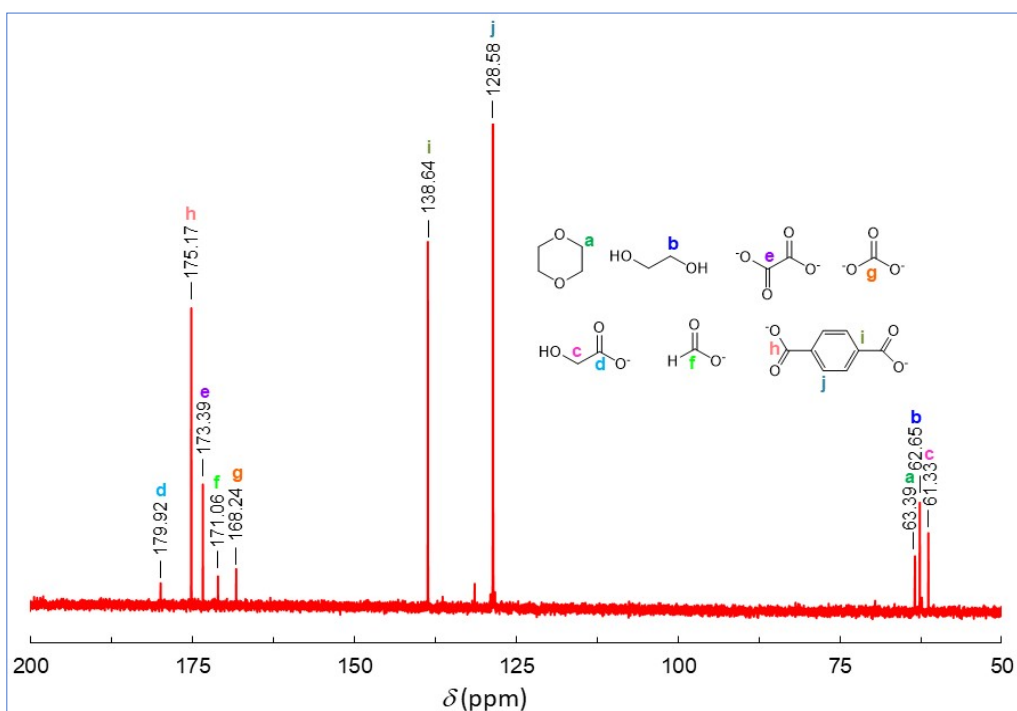




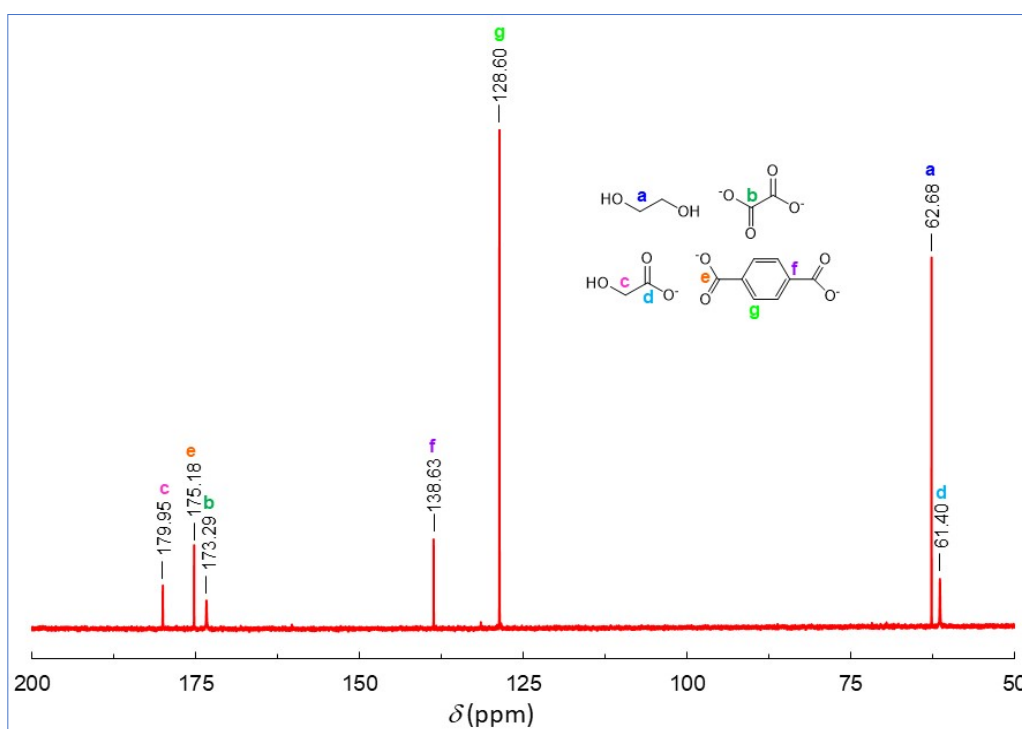
**Figure S10.** Top: <sup>1</sup>H-NMR spectrum of PET Hydrolysate in pH 14 before electrolysis. Bottom: <sup>1</sup>H-NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of PET Hydrolysate at pH 14. Experimental conditions: carbon cloth (1x1 cm<sup>2</sup>), graphite rod, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. Dioxane is used as an internal standard. [EG] = 0.825 mM, [TEMPO] = 15 mM, Dioxane = 100%.



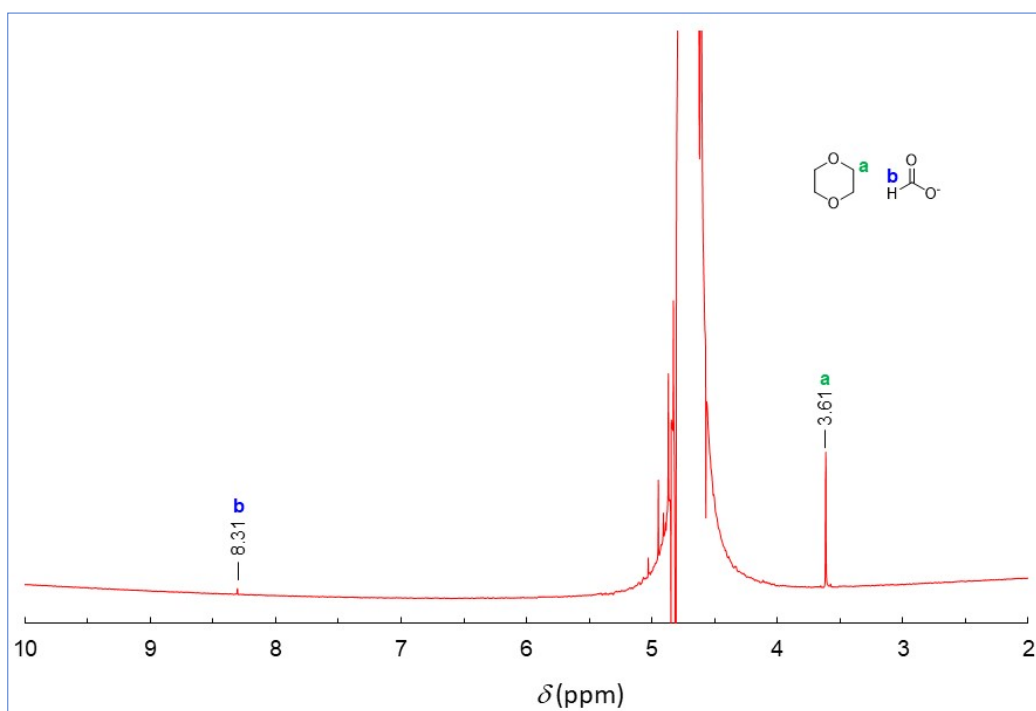
**Figure S11.** Top: <sup>1</sup>H-NMR spectrum of PET Hydrolysate in pH 10 before electrolysis. Bottom: <sup>1</sup>H-NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of PET Hydrolysate at pH 10. Experimental conditions: carbon cloth (1x1 cm<sup>2</sup>), graphite rod, and Ag/AgCl were used as the working, counter, and reference electrodes. Dioxane is used as an internal standard. [EG] = 0.654 mM, [TEMPO] = 15 mM, Dioxane = 100%.



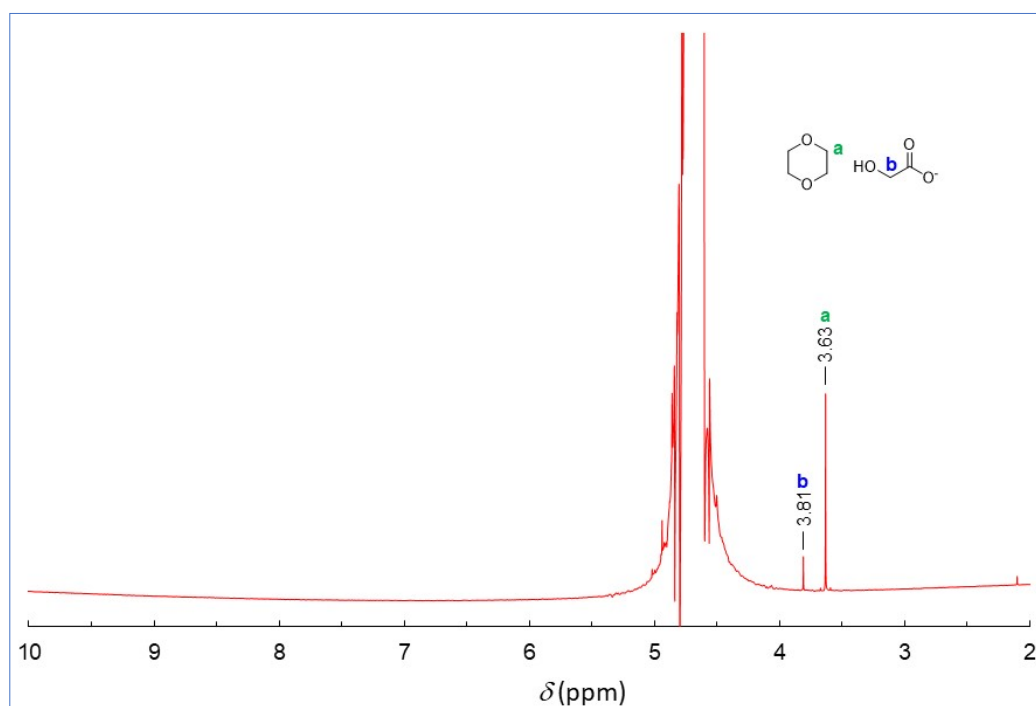
**Figure S12.**  $^{13}\text{C}$ -NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of PET Hydrolysate at pH 14. Experimental conditions: carbon cloth ( $1 \times 1 \text{ cm}^2$ ), graphite rod, and Ag/AgCl were used as the working, counter, and reference electrodes.  $[\text{EG}] = 0.825 \text{ mM}$ ,  $[\text{TEMPO}] = 15 \text{ mM}$ , Dioxane = 100%



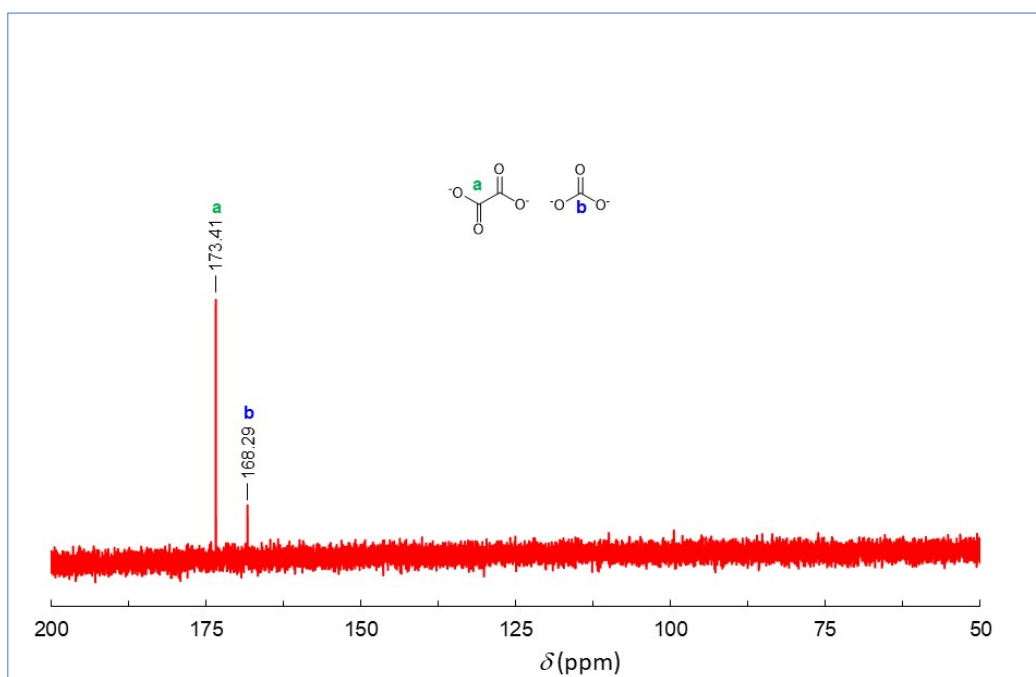
**Figure S13.**  $^{13}\text{C}$ -NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of PET Hydrolysate at pH 10. Experimental conditions: carbon cloth ( $1 \times 1 \text{ cm}^2$ ), graphite rod, and Ag/AgCl were used as the working, counter, and reference electrodes.  $[\text{EG}] = 0.654 \text{ mM}$ ,  $[\text{TEMPO}] = 15 \text{ mM}$ .



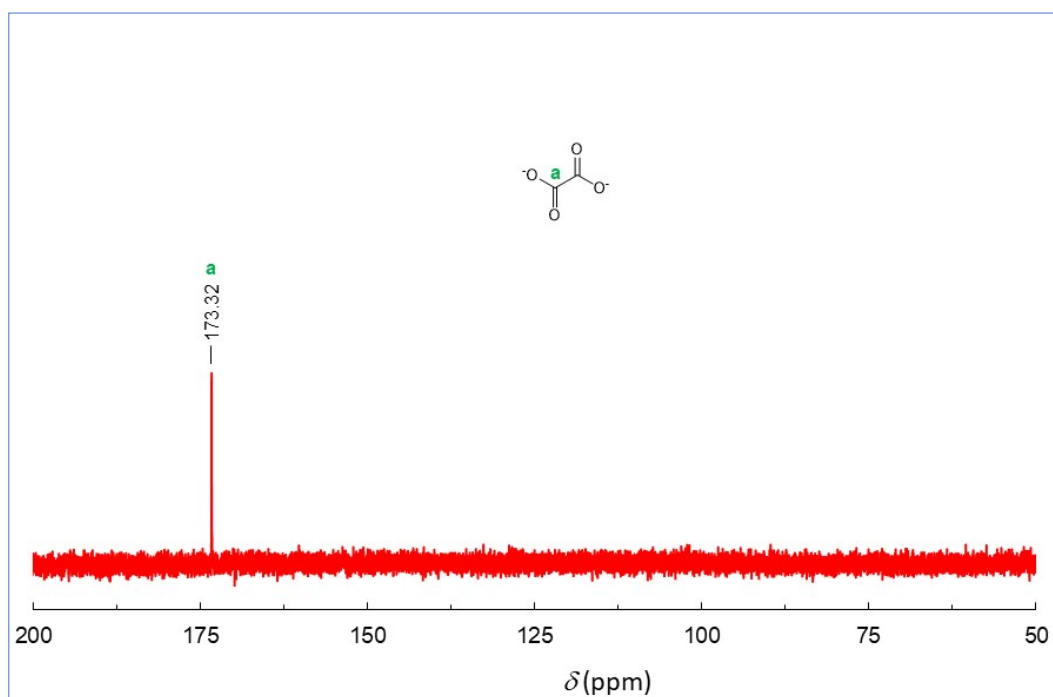
**Figure S14.** <sup>1</sup>H-NMR spectra of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of SG at pH 14. Experimental conditions: carbon cloth (1x1 cm<sup>2</sup>), Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes. Dioxane is used as an internal standard. [SG]= 30 mM, [TEMPO] = 7.5 mM, Dioxane = 12.5%



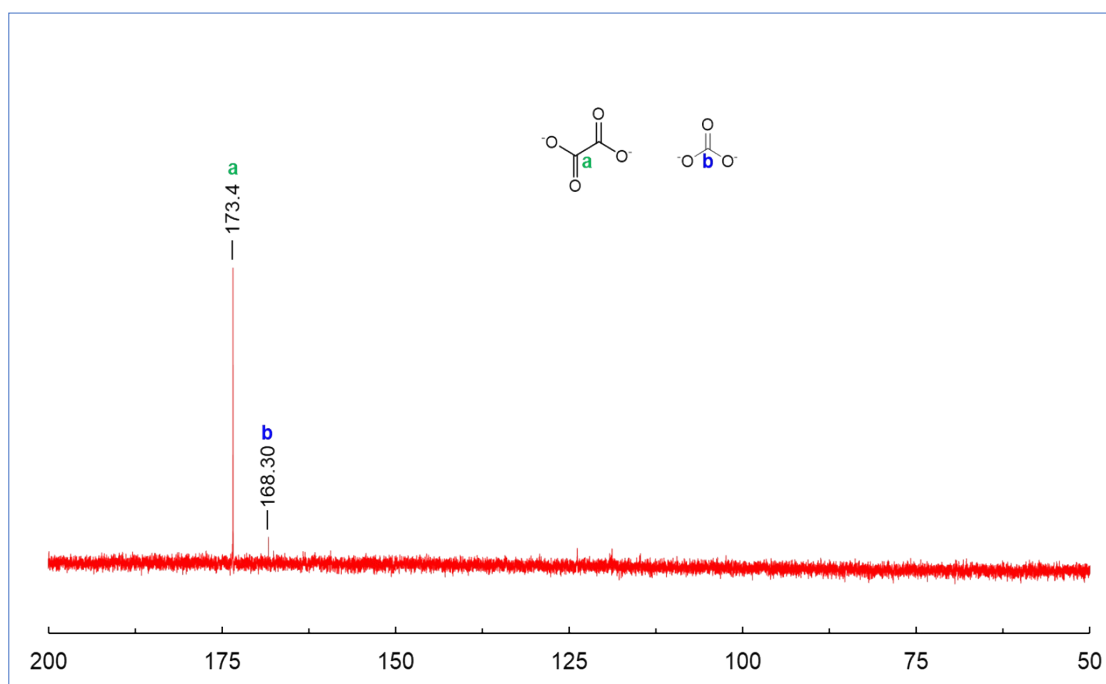
**Figure S15.** <sup>1</sup>H-NMR spectra of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of SG at pH 10. Experimental conditions: carbon cloth (1x1 cm<sup>2</sup>), Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes. Dioxane is used as an internal standard. [SG] = 30 mM, [TEMPO] = 7.5 mM, Dioxane = 12.5%



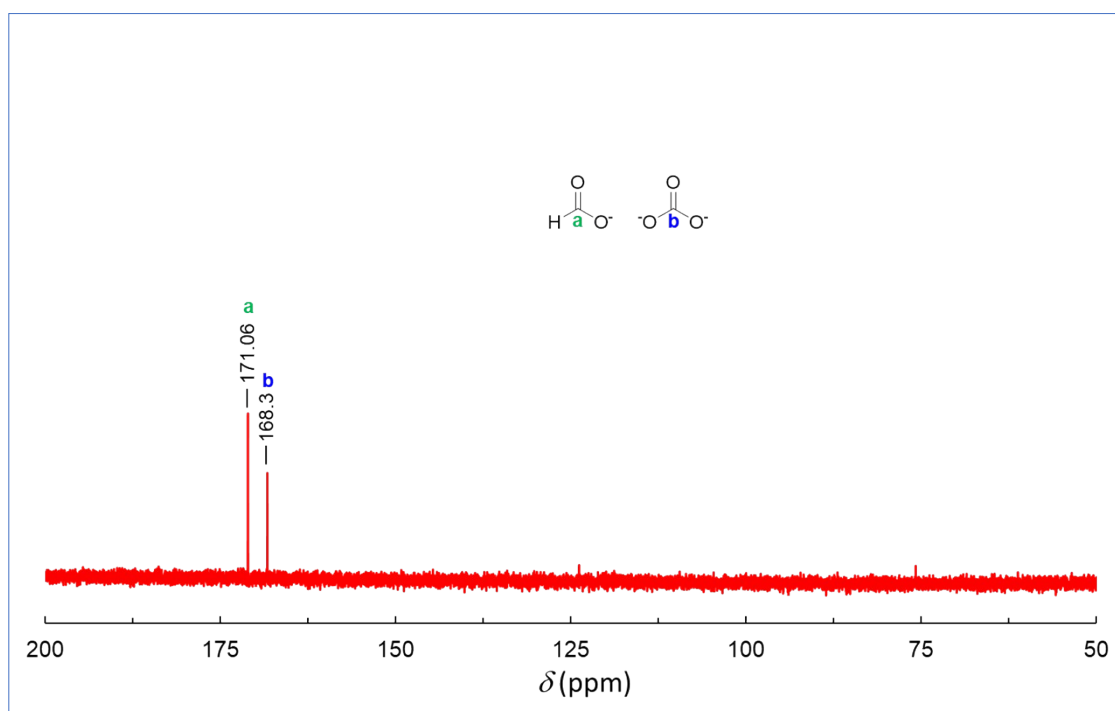
**Figure S16.** <sup>13</sup>C-NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of SG at pH 14. Experimental conditions: carbon cloth (1x1 cm<sup>2</sup>), Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes.



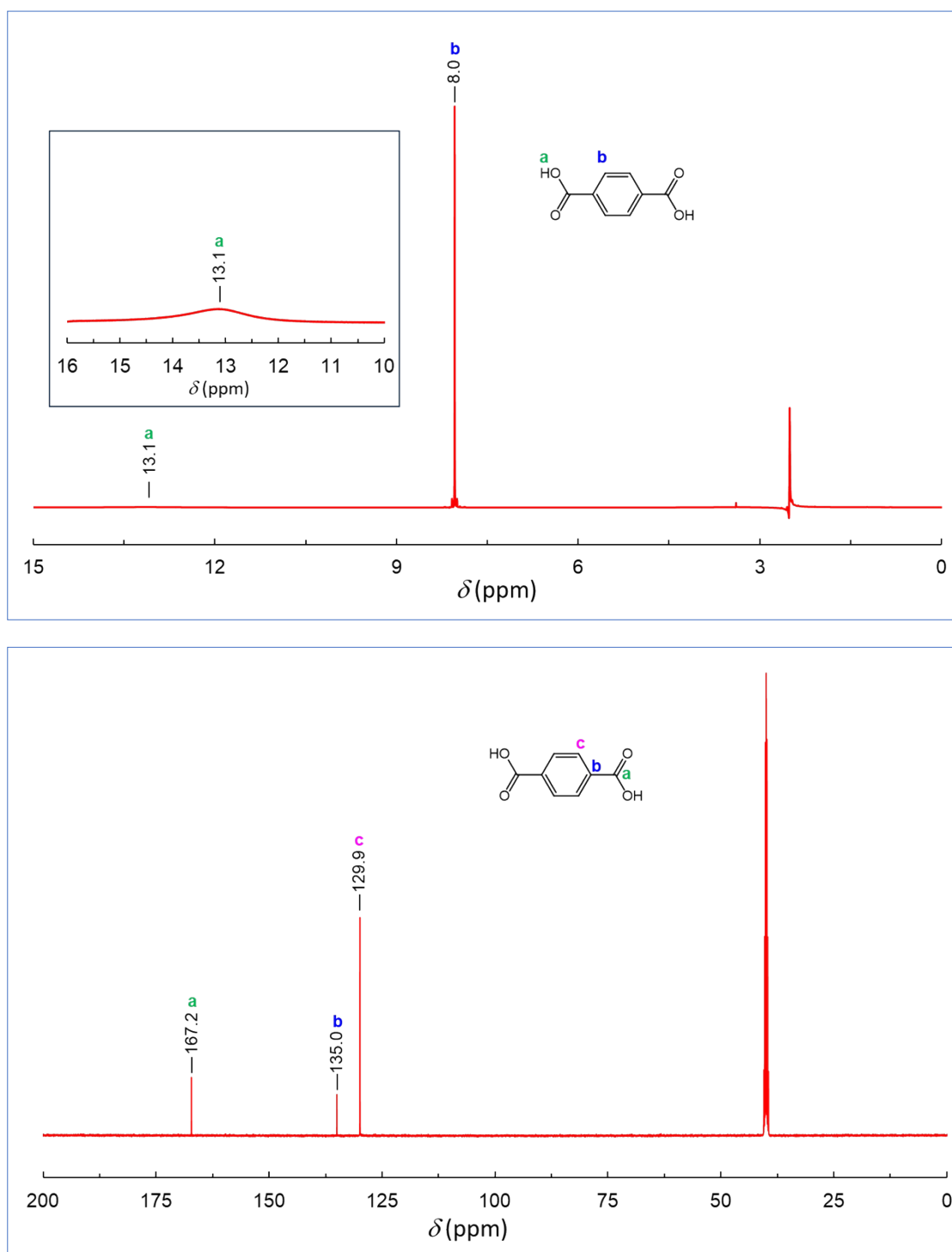
**Figure S17.** <sup>13</sup>C-NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of SG at pH 10. Experimental conditions: carbon cloth (1x1 cm<sup>2</sup>), Pt wire, and Ag/AgCl were used as the working, counter, and reference electrodes.



**Figure S18.**  $^{13}\text{C}$ -NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of oxalate at pH 14.



**Figure S19.**  $^{13}\text{C}$ -NMR spectrum of the post-electrolysis sample of TEMPO-mediated bulk electrolysis of formate at pH 14.



**Figure S20.** Top: <sup>1</sup>H-NMR spectrum of isolated TPA after electrolysis (Inset: signal for carboxylic acid protons in isolated TPA). Bottom: <sup>13</sup>C-NMR spectrum of TPA isolated from the post-electrolysis sample of TEMPO-mediated bulk electrolysis of PET Hydrolysate.

**Table S2a.** Product selectivity of TEMPO-mediated Ethylene glycol (EG) oxidation.

| pH | Potential (V vs. NHE) | Set of expt. | EG (%) | Glycolate (%) | Formate (%) | Oxalate | Carbonate |
|----|-----------------------|--------------|--------|---------------|-------------|---------|-----------|
| 10 | 0.77                  | 1.           | 28     | 35            | ☐           | ☐       | ☐         |
|    |                       | 2.           | 29.2   | 35.5          | ☐           | ☐       | ☐         |
|    | 0.94                  | 1.           | 22.5   | 42.5          | ☐           | ☐       | ☐         |
|    |                       | 2.           | 24     | 39            | ☐           | ☐       | ☐         |
| 14 | 0.79                  | 1.           | 7.5    | 17            | 6           | ☐       | ☐         |
|    |                       | 2.           | 10     | 23            | 7           | ☐       | ☐         |
|    | 0.84                  | 1.           | 9      | 24            | 8           | ☐       | ☐         |
|    |                       | 2.           | 15     | 29            | 5           | ☐       | ☐         |
|    | 0.94                  | 1.           | 6      | 11            | 5           | ☐       | ☐         |
|    |                       | 2.           | 7.5    | 16            | 5           | ☐       | ☐         |

**Table S2b.** Product selectivity of TEMPO-mediated Sodium glycolate (SG) oxidation.

| pH | Potential (V vs. NHE) | Set of expt. | Glycolate (%) | Formate (%) | Oxalate | Carbonate |
|----|-----------------------|--------------|---------------|-------------|---------|-----------|
| 10 | 0.94                  | 1.           | 11            | ☐           | ☐       | ☐         |
|    |                       | 2.           | 6.5           | ☐           | ☐       | ☐         |
| 14 | 0.94                  | 1.           | -             | 4           | ☐       | ☐         |
|    |                       | 2.           | -             | 3           | ☐       | ☐         |

**Table S2c.** Product selectivity of TEMPO-mediated oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) oxidation.

| pH | Potential (V vs. NHE) | Set of expt. | Formate (%) | Oxalate | Carbonate |
|----|-----------------------|--------------|-------------|---------|-----------|
| 14 | 0.94                  | 1.           | 3           | ☐       | ☐         |
|    |                       | 2.           | 4           | ☐       | ☐         |

**Table S2d.** Product selectivity of TEMPO mediated formate (HCOO<sup>-</sup>) oxidation.

| pH | Potential (V vs. NHE) | Set of expt. | Formate (%) | Carbonate |
|----|-----------------------|--------------|-------------|-----------|
| 14 | 0.94                  | 1.           | ☐           | ☐         |

**Table S2e.** Product selectivity of TEMPO-mediated PET hydrolysate oxidation.

| pH | Potential (V vs. NHE) | EG (%) | Glycolate (%) | Formate (%) | Oxalate | Carbonate |
|----|-----------------------|--------|---------------|-------------|---------|-----------|
| 10 | 0.94                  | 23.03  | 42.9          | ☐           | ☐       | ☐         |
| 14 | 0.94                  | 17.10  | 25            | 8.72        | ☐       | ☐         |



**Table S3.** The total mass balance and %Faradaic yield for the reactions considering a particular batch.

| EGOR at ~ 0.9 V vs. NHE  |             |                  |               |             |             |               |                   |
|--------------------------|-------------|------------------|---------------|-------------|-------------|---------------|-------------------|
| pH                       |             | Unreacted EG (%) | Glycolate (%) | Formate (%) | Oxalate (%) | Carbonate (%) | Mass Balance      |
| 10                       | % NMR yield | 22.5             | 42.5          | x           | 9.86        | x             | 74.86             |
|                          | % FY        | -                | 43.77         | x           | 20.34       | x             | Total %FY = 64.11 |
| 14                       | % NMR yield | 7.5              | 16            | 5           | 12.19       | 14.49         | 55.18             |
|                          | % FY        | -                | 16.48         | 3.85        | 25.12       | 18.6          | Total %FY = 64.05 |
| PETOR at ~ 0.9 V vs. NHE |             |                  |               |             |             |               |                   |
| 10                       | % NMR yield | 23.03            | 42.9          | x           | 4.51        | x             | 70.44             |
|                          | % FY        | -                | 44.11         | x           | 9.27        | x             | Total %FY = 53.38 |
| 14                       | % NMR yield | 17               | 25            | 8.72        | 18.7        | 10.42         | 79.84             |
|                          | % FY        | -                | 25.12         | 6.56        | 37.57       | 13.08         | Total %FY = 82.33 |

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy were used to quantify the products during the electrolysis process. The NMR samples for EGOR were prepared by taking 150  $\mu\text{L}$  sample with 1,4-Dioxane (equi-millimoles of the substrate) + 450  $\mu\text{L}$   $\text{D}_2\text{O}$  for  $^1\text{H}$ ; 450  $\mu\text{L}$  sample with 1,4-Dioxane (equi-millimoles of the substrate) + 150  $\mu\text{L}$   $\text{D}_2\text{O}$  for  $^{13}\text{C}$ , and for PET Hydrolysate oxidation: 100  $\mu\text{L}$  sample + 100  $\mu\text{L}$  1,4-Dioxane in pH buffer (as internal standard) + 400  $\mu\text{L}$   $\text{D}_2\text{O}$ .

The quantification of the products from  $^1\text{H}$  NMR was measured by using equation 3.<sup>1</sup>

$$m_{\text{product}} = \frac{I_{\text{product}} \times N_{1,4\text{-Dioxane}} \times M_{\text{product}}}{I_{1,4\text{-Dioxane}} \times N_{\text{product}} \times M_{1,4\text{-Dioxane}}} \times m_{1,4\text{-Dioxane}} \times n$$

(Equation S3)

Where  $I_{\text{product}}$  and  $I_{1,4\text{-Dioxane}}$  is the integral of product peak and 1,4-Dioxane, respectively,  $N_{\text{product}}$  and  $N_{1,4\text{-Dioxane}}$  is the numbers of protons corresponding to product peak and 1,4-dioxane peak, respectively,  $M_{\text{product}}$  and  $M_{1,4\text{-Dioxane}}$  is the molar mass of product and 1,4-dioxane, respectively.  $m_{\text{product}}$  and  $m_{1,4\text{-Dioxane}}$  is the mass of product and 1,4-Dioxane, respectively,  $n = 10 \text{ mL}/100 \mu\text{L} = 100$ .

After product quantification from  $^1\text{H-NMR}$ , for pH 14 carbonate and oxalate quantification, formate was considered as pseudo internal standard, and for pH 10 oxalate quantification, residual ethylene glycol was considered as pseudo internal standard (as calculated from  $^1\text{H NMR}$ ) in the  $^{13}\text{C-NMR}$  of EGOR and PET Hydrolysate oxidation by using the following equation 4.

$$m_{\text{product}} = \frac{I_{\text{product}} \times N_{\text{int std}} \times M_{\text{product}}}{I_{\text{int std}} \times N_{\text{product}} \times M_{\text{int std}}} \times m_{\text{int std}} \quad (\text{Equation S4})$$

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