

1 **SUPPORTING INFORMATION**

2
3 **Novel Conductive and Redox-Active Molecularly Imprinted Polymer for Direct**
4 **Quantification of Perfluorooctanoic Acid**

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21
22 **16 pages**

23 **4 tables**

24 **8 figures**

25 **6 textes**

26

27 **Text S1:** Chemical and Reagents

28 3,4-ethylenedioxythiophene hydroxymethyl (EDOT-MeOH, $\geq 95\%$), 4-carboxy-2,2,6,6-tetra
29 methylpiperidinyloxy (TEMPO-COOH, $\geq 97\%$), 4-(dimethylamino)pyridine (DMAP, $\geq 99\%$), *N*-
30 (3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC, $\geq 97\%$) and anhydrous
31 dichloromethane (DCM, $\geq 99\%$), were obtained from TCI (Tokyo, Japan) and used as received.
32 Sodium chloride (NaCl, $\geq 99.5\%$) was purchased from Fisher Scientific (Pittsburgh, PA) and used
33 as received. Perfluorooctanoic acid (PFOA, $\geq 97\%$), perfluorobutanoic acid (PFBA, $\geq 98\%$),
34 Perfluorooctanesulfonic acid solution (PFOS, $\geq 97\%$), dry tetrabutylammonium
35 hexafluorophosphate (TBAPF₆, $\geq 99\%$), phenylhydrazine (97%), anhydrous magnesium sulfate
36 (MgSO₄, $\geq 99.7\%$), hexane (99.9%, HPLC Grade), dichloromethane (99.9%, HPLC Grade), and
37 ethyl acetate (99.9%, HPLC Grade) were purchased from Sigma-Aldrich (Milwaukee, MI) and
38 used as received. 6:2 Fluorotelomer sulfonamide alkylbetaine (6:2 FTAB, $\geq 97\%$) was obtained
39 from TRC (Connecticut, USA). Suwannee River natural organic matter (SRNOM) was purchased
40 from the International Humic Substances Society (IHSS, MN, USA). Deionized (DI) water was
41 purified by a Mili-Q-plus purification system (≥ 18.2 M Ω cm at 25 °C; Millipore Sigma, MO,
42 USA). Surface water (SW) was collected from a pond (latitude and longitude of 40.310329 and -
43 74.644513°, respectively) in West Windsor Township, New Jersey. The sampling location and the
44 surface water composition are provided in **Figure S7** and **Table S3**.

45 **Text S2:** Material Characterization.

46 ¹H nuclear magnetic resonance (NMR) spectra were recorded for EDOT-TEMPO monomer at
47 25 °C on a JEOL ECZ400S, 400 MHz spectrometer using deuterated chloroform as a solvent and
48 tetramethyl silane as an internal standard. Fourier Transform Infrared Spectroscopy measurements

49 (FTIR) were recorded on a Perkin Elmer 1600 Series FTIR Spectrophotometer. The spectrum was
50 collected in 32 scans with a resolution of 4 cm^{-1} in the $4000\text{-}400\text{ cm}^{-1}$ range.

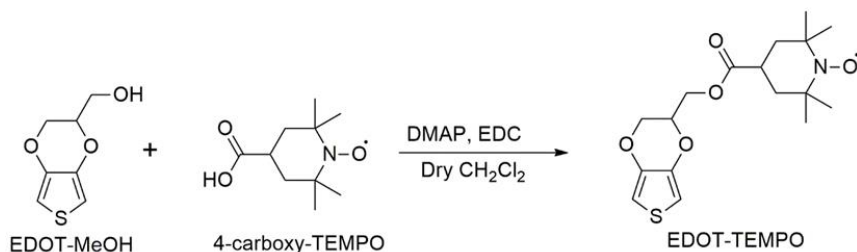
51 **Text S3:** Chemical Analysis

52 The non-purgeable organic carbon (NPOC) was analyzed with a TOC analyzer (TOC-L,
53 Shimadzu, Japan). The cations (Na^+ , K^+ , Mg^+ , and Ca^+) and anions (Cl^- and SO_4^{2-}) were analyzed
54 with an ion chromatography (IC) coupled with a conductivity detector using a Shodex YS-50
55 column (for cations) or Shodex SI-52 4E column (for anion) (Showa Denko, Tokyo, Japan),
56 respectively. The turbidity and conductivity of the surface water sample was measured on a
57 turbidity meter (2100Q, HACH) and a conductivity meter (HQ40d, HACH), respectively. PFAS
58 analysis was performed on an Agilent 6470A triple quadrupole LC/MS (LC/QQQ-MS) system
59 C18 column (Agilent poroshell 120 EC, $50 \times 3\text{ mm}$, $1.8\text{ }\mu\text{m}$) with the mobile phases of solvent A
60 (5 mM ammonium acetate in distilled water) and B (5 mM ammonium acetate in 100% methanol).
61 The oven temperature was set at $40\text{ }^\circ\text{C}$. The injection volume of each sample was $5\text{ }\mu\text{L}$ with a flow
62 rate of $0.5\text{ ml}\cdot\text{min}^{-1}$. Prior to analysis, all samples were filtered by $0.22\text{-}\mu\text{m}$ PES filters with 1-mL
63 syringes into polypropylene 1.5-mL autosampler vials (ThermoFisher) with polypropylene caps.
64 An Agilent 6470A triple quadrupole LC-/MS/MS system was used to detect quantify the
65 concentrations of EPA 537 standards, EPA 533 standards, and intermediates (C2 ~ C7) based on
66 USEPA Method 533 following mass calibration and initial calibration. Analytical sequences will
67 include instrument blanks, instrument sensitivity checks, calibration verification standards,
68 qualitative identification standards, method blanks, ongoing precision and recovery standards
69 (OPRs), and experimental samples. A C18 column (Agilent poroshell 120 EC, $50 \times 3\text{ mm}$, $1.8\text{ }\mu\text{m}$)
70 was used for separation at $40\text{ }^\circ\text{C}$ using a mobile phase of solvent A (5 mM ammonium acetate in
71 distilled water) and B (5 mM ammonium acetate in 100% methanol). The injection volume of each

72 sample is 5 μL with a flow rate of $0.5 \text{ ml}\cdot\text{min}^{-1}$. The EPA 533 standard (500 ppb) (Lot
73 No.537PDSLRL11021) purchased from Wellington laboratories were diluted with 100% methanol
74 to, 100 ppt, 250 ppt, 500 ppt, 1 ppb, 2.5 ppb, 5 ppb, 10 ppb, 25 ppb and 50 ppb, respectively, to
75 establish the calibration curve.

76 **Text S4:** Preparation of MIPs.

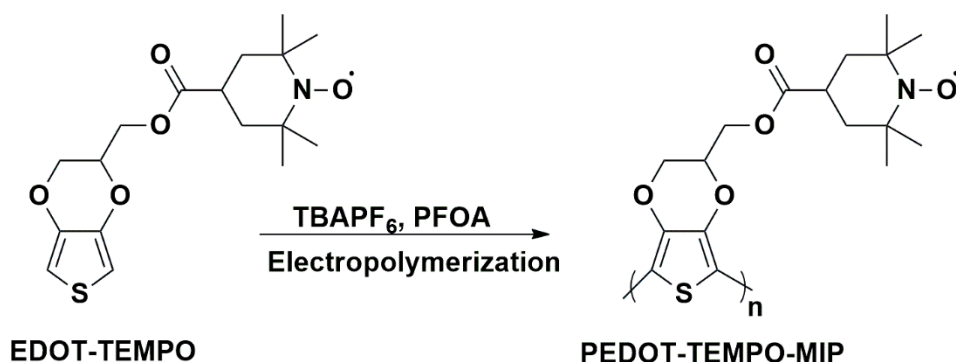
77 **Synthesis and purification of 3,4-ethylenedioxythiophene-2,2,6,6-tetramethyl piperidinyloxy**
78 **(EDOT-TEMPO) monomer.** We prepared the 3,4-ethylenedioxythiophene-2,2,6,6-
79 tetramethylpiperidinyloxy (EDOT-TEMPO) monomer by the esterification reaction between 3,4-
80 ethylenedioxythiophene hydroxymethyl and 4-carboxy-2,2,6,6-tetramethyl piperidinyloxy in the
81 presence of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimidehydrochloride (EDC) and 4-
82 (dimethylamino) pyridine under dry dichloromethane (DCM) following the **Scheme S1**.^{3,4} Briefly,
83 TEMPO-COOH (1.4 mmol, 280 mg,) EDOT-MeOH (2.18 mmol, 380 mg), and DMAP (1.34
84 mmol, 17 mg) were dissolved in 10 mL of dry DCM in a 100 mL round bottom flask for 5 minutes
85 under stirring at 0 °C. After 5 min, EDC (1.52 mmol, 310 mg) was dissolved in 4 mL of dry DCM
86 and added dropwise into the round bottom flask at 0°C under stirring. The reactor was then warmed
87 up to room temperature and stirred for 72 h. After 72 h, the reaction solution was diluted with 20
88 mL DCM, and the organic phase was washed with NaCl (40 mL) and water (80 mL), then dried
89 over anhydrous MgSO_4 and filtered using 11 μm Whatman paper. The filtrate was purified by
90 column chromatography (SiO_2 , *n*-hexane/ethyl acetate 1:3 volume ratio) and followed by
91 recrystallization in cold *n*-hexane. The obtained EDOT-TEMPO monomer appeared as orange
92 color crystals, as shown in **Figure S2**. For ^1H NMR analysis, phenylhydrazine was added to reduce
93 the nitroxide free radical to its hydroxylamine derivative.



95 **Scheme S1.** Scheme for the synthesis of EDOT-TEMPO monomer via the esterification reaction
 96 between EDOT-MeOH and TEMPO-COOH at room temperature for 72 h.

97 **Electrochemical polymerization of poly-3,4-ethylenedioxythiophene-2,2,6,6-**
 98 **tetramethylpiperidinyloxy (PEDOT-TEMPO-MIP) and non-molecularly imprinted**
 99 **polymers (PEDOT-TEMPO-NIP).** PEDOT-TEMPO-MIP and PEDOT-TEMPO-NIP were
 100 prepared by the electrochemical polymerization of EDOT-TEMPO monomer following a method
 101 established from previous studies.^{1,2} The reaction scheme was shown in **Scheme S2**. The glassy
 102 carbon electrode was first polished using 0.3 and 0.05 μm alumina slurry and washed using
 103 deionized water for 5 min under a sonication bath. A standard three-electrode configuration was
 104 employed with a 3 mm glassy carbon working electrode (BASi, IN, USA), a coiled platinum wire
 105 counter electrode (BASi, IN, USA), and an Ag/AgCl reference electrode in 3 M KCl (BASi, IN,
 106 USA). All potentials were applied against Ag/AgCl reference electrode in 0.1 mol·L⁻¹ TBAPF₆
 107 DCM solution. A CH Instruments 630C potentiostat (Austin, TX) was used for electrochemical
 108 polymerization and PFOA quantification. Specifically, the electrochemical polymerization of the
 109 EDOT-TEMPO (1 mmol·L⁻¹) was performed in 0.1 mol·L⁻¹ TBAPF₆ in DCM at a scan rate of 20
 110 mV·s⁻¹ for 10 sweep cycles on the surface of the glassy electrode under cyclic voltammetry (CV)
 111 with a potential range from 0-1.5 V. MIPs were prepared in the presence of 1 mmol·L⁻¹ of PFOA,
 112 whereas NIP was synthesized under the same condition except in the absence of PFOA. After the
 113 completion of the electrochemical polymerization, the electrode was washed with deionized water

114 to remove the PFOA template. Herein, we have chosen DI water for PFOA template removal
115 because organic solvents such as methanol, ethanol, and acetone can dissolve PEDOT-TEMPO-
116 MIP.³⁻⁵ Moreover, the use of DI for template removal and MIP regeneration is also cost-effective
117 compared to other technologies where organic solvents are often employed.



119 **Scheme S2.** Scheme for the synthesis of PEDOT-TEMPO-MIP using 1 mmol·L⁻¹ EDOT-TEMPO
120 and 1 mmol·L⁻¹ PFOA in a 0.1 M TBAPF₆ dichloromethane solution, employing a scan rate of 20
121 mV·s⁻¹ and a potential range of 0-1.5 V.

122 **Text S5:** Method Detection Limit (MDL) calculation

123 The MDL was calculated using the standard deviation (SD) of seven replicates at the lowest PFOA
124 concentration used for the rebinding experiments (i.e., 4.14×10⁻¹⁰ g·L⁻¹ and 4.14×10⁻⁹ g·L⁻¹)
125 following an EPA standard method.^{6,7} Specifically, the standard deviation of the measured
126 concentrations of seven replicates were determined using the calibration curve (i.e., Figure 2,
127 R²=0.98), and the MDL was calculated following the equation below:

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$$\text{MDL} = (n-1, 1-\alpha=0.99) \cdot \text{SD}$$

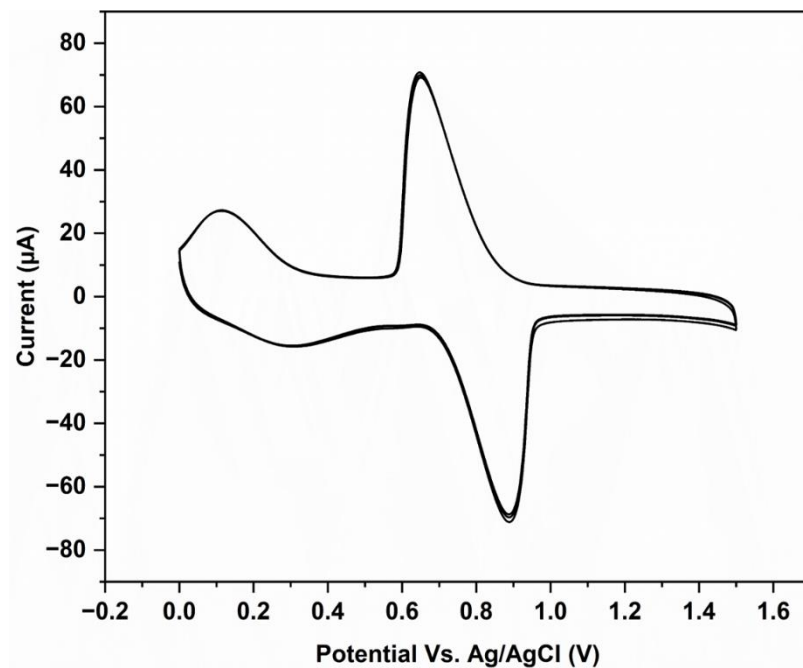
129 where MDL represents the method detection limit, $t_{(n-1, 1-\alpha=0.99)}$ represents Student's t-value for a
130 single tailed 99th percentile at the degrees of freedom of 6, and SD represents the standard deviation
131 derived from 7 replicates.

132 **Text S6:** Characterization of EDOT-TEMPO monomer

133 The ¹H NMR spectrum (**Figure S3**) of EDOT-TEMPO shows two distinctive resonance peaks at
134 4.6 and 4.2 ppm corresponding to the methylene protons adjacent to carbonyl carbon bonded to
135 the ester oxygen (-CH₂-COO-), suggesting the successful esterification of EDOT-MeOH and
136 TEMPO-COOH.^{44,45} The resonance at 1.2, 1.4, 1.8, and 2.6 ppm represent the TEMPO-COOH
137 protons, while those at 6.4 and 3.9 ppm correspond to the EDOT-MeOH protons.^{44,45} The
138 resonance peaks at 6.8 and 7.15 ppm (crossed out in red) represent the phenylhydrazine protons,
139 which were used to reduce the nitroxide free radical to its hydroxyl derivative.^{44,45} Our FTIR results
140 further support these observations (**Figure S4**). Specifically, the vibrational stretching peak shift
141 from 1690 cm⁻¹ to 1732 cm⁻¹ corresponds to the conversion of carboxylic carbonyl to ester
142 carbonyl. The disappearance of the hydroxyl peak at 3200 cm⁻¹ indicates successful esterification
143 of EDOT-MeOH and TEMPO-COOH.^{44,45}

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147 **Figure S1.** Three cycles of cyclic voltammograms (CV) scans of PEDOT-TEMPO-MIP after
148 template removal in 0.1 M TBAPF₆ dichloromethane solution.

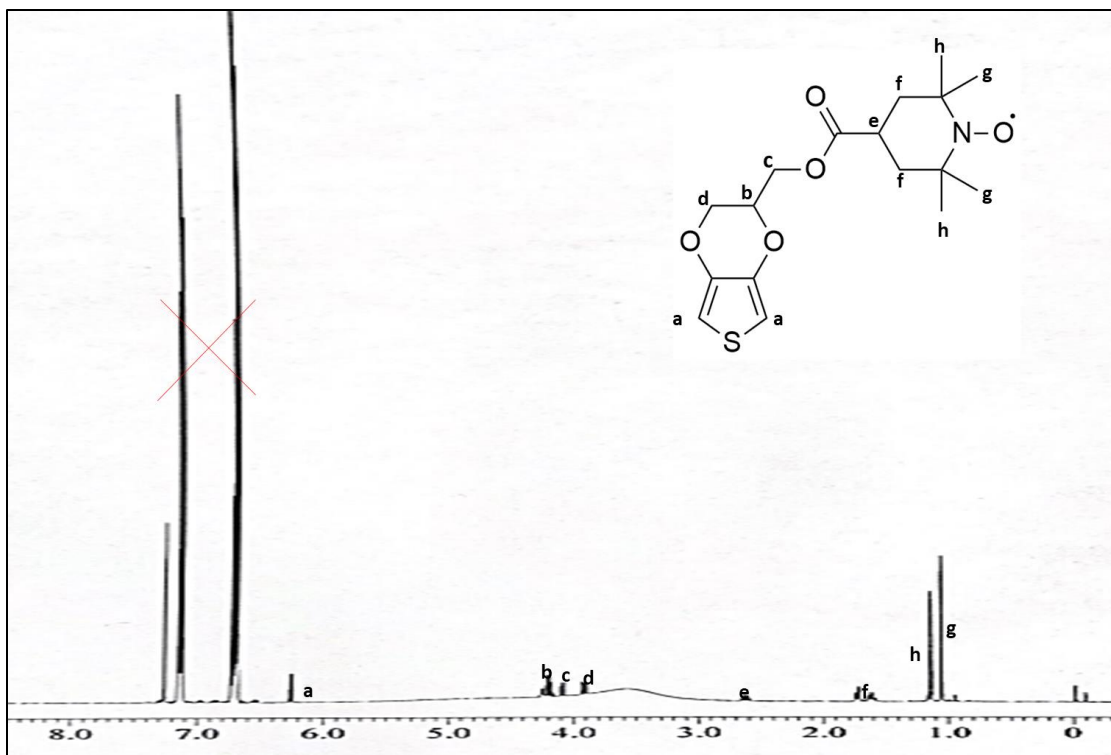


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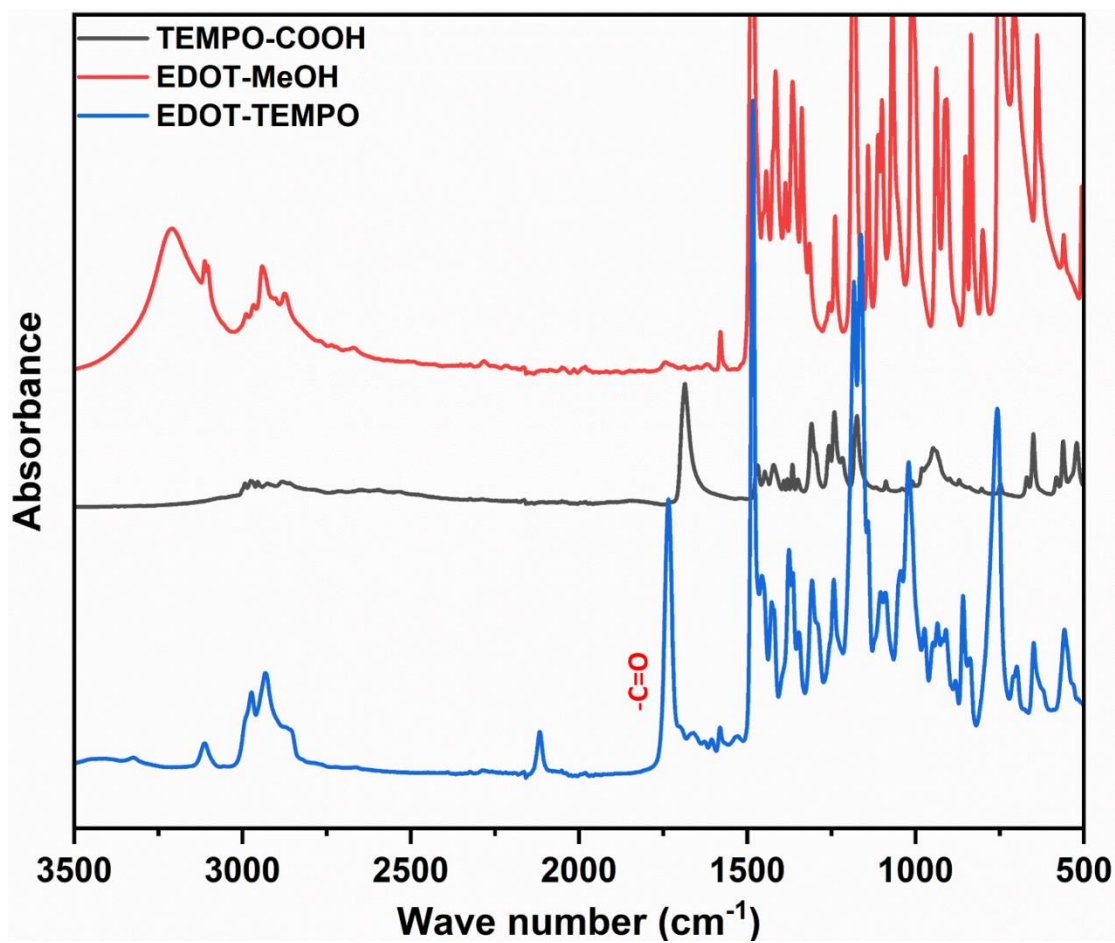
151 **Figure S2.** Orange color crystal of EDOT-TEMPO monomer after purification.

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154 **Figure S3.** ¹H NMR spectrum of EDOT-TEMPO synthesized *via*. the condensation reaction of
 155 EDOT-MeOH and TEMPO-COOH at room temperature for 72 h.

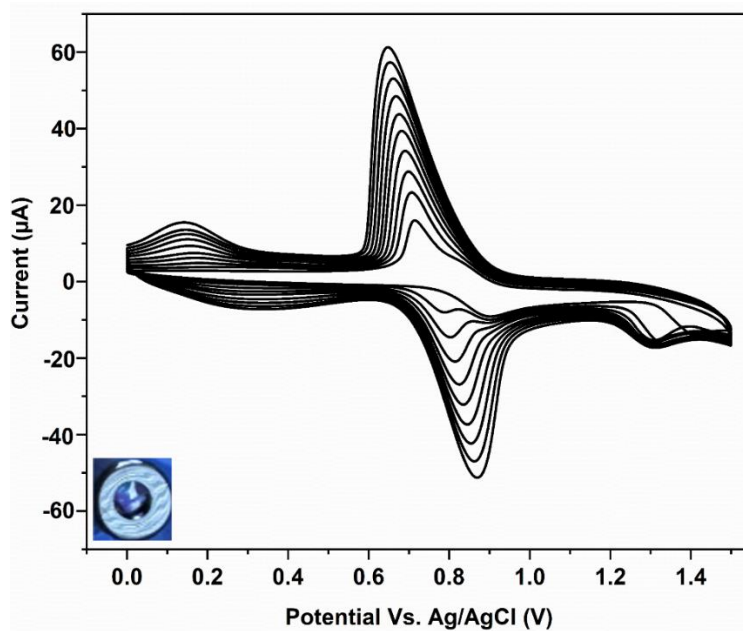


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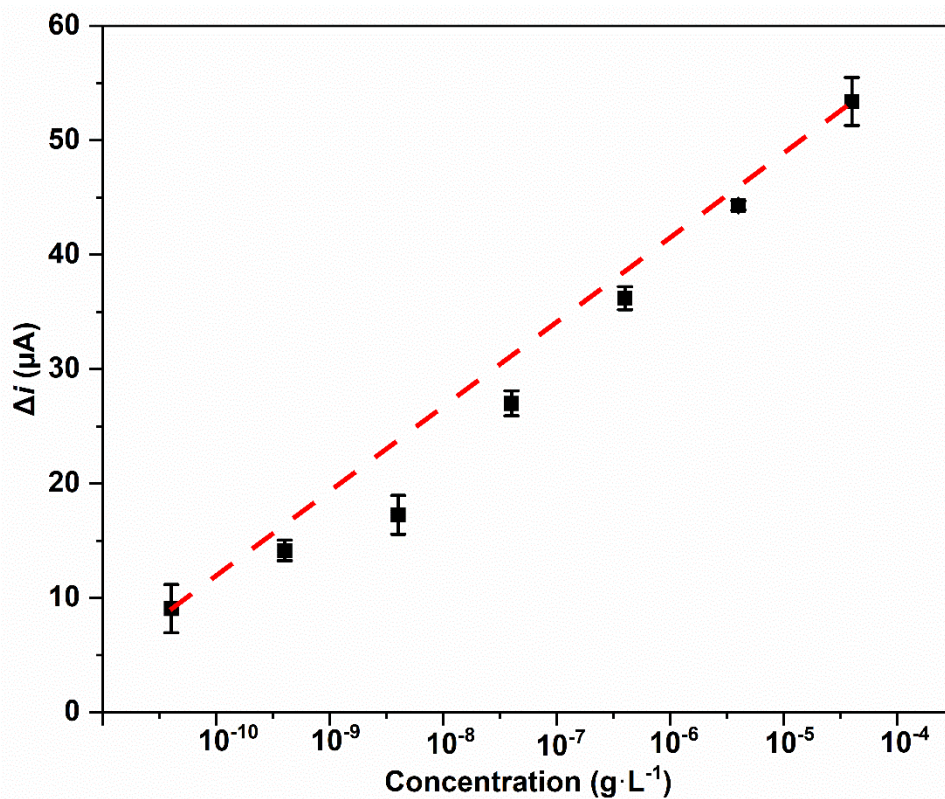
157 **Figure S4.** FTIR spectrum of EDOT-TEMPO synthesized *via.* the condensation reaction of
158 EDOT-MeOH and TEMPO-COOH at room temperature for 72 h.

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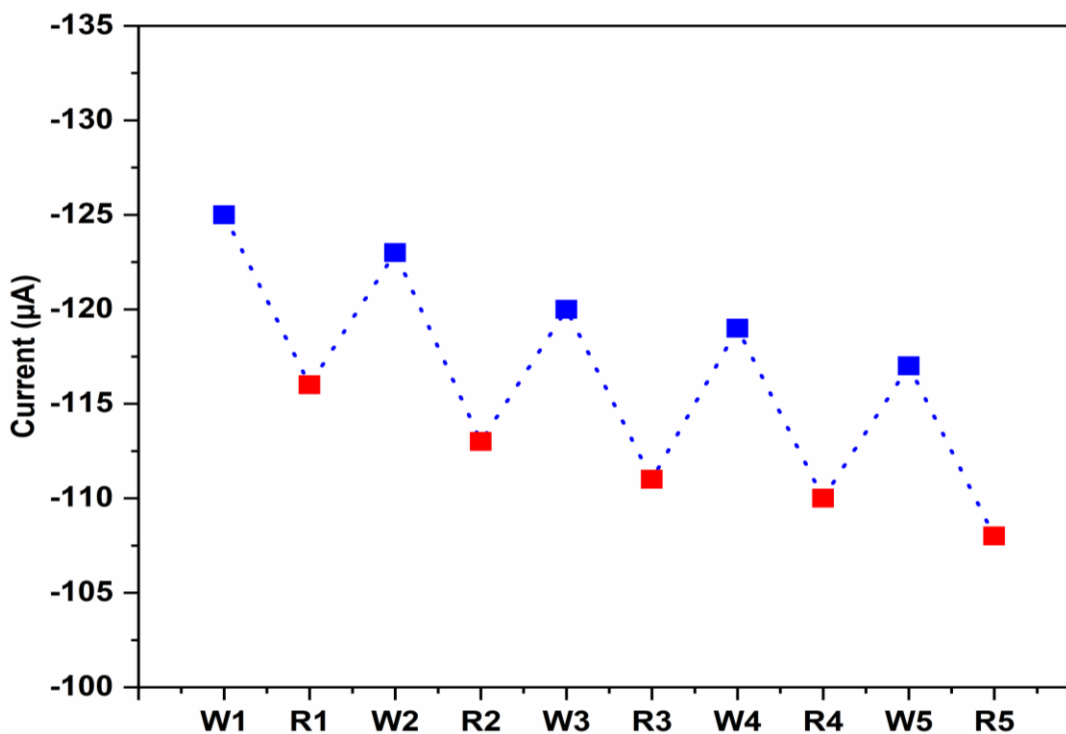
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 162 **Figure S5.** Ten cycles of CV scans during electropolymerization of PEDOT-TEMPO-MIP using
 163 EDOT-TEMPO in 0.1 M TBAPF₆ dichloromethane solution. The scan rate was at 20 mV·s⁻¹ and
 164 the potential used range from 0-1.5 V. The inset image shows the blue color film deposited after
 165 electropolymerization.



167 **Figure S6.** The calibration curve of the current density decreases at the anodic peak of TEMPO
168 (y-axis) vs. PFOA concentrations ranging from 4.14×10^{-10} to $4.14 \times 10^{-4} \text{ g} \cdot \text{L}^{-1}$ (x-axis). The current
169 density was recorded from the CV scans of PEDOT-TEMPO-MIP after being exposed to PFOA
170 for 240 minutes. The error bar at each point was derived from triplicate measurements. The linear
171 regression is $y = 0.75x - 0.15$ ($R^2 = 0.98$).



172
173 **Figure S7.** The relative changes in the current density of TEMPO's anodic peak at 0.87 V over 5
174 cycles of washing (template removal) and rebinding (when exposed to $4.14 \times 10^{-9} \text{ g} \cdot \text{L}^{-1}$ PFOA).
175 Results from the washing and rebinding cycles are abbreviated as RX and WX, where X represents
176 the number of cycles.



177
 178 **Figure S8.** The sampling location of the surface water from a pond near West Windsor Township,
 179 New Jersey, USA (40.310329°, -74.644513°).

180 **Table S1.** The decrease in current density of the anodic peak of TEMPO during PFOA rebinding
 181 at different time intervals.

Time (minutes)	$\Delta i / i_0\%$ ($4.14 \times 10^{-4} \text{ g} \cdot \text{L}^{-1}$ ¹ PFOA)	$\Delta i / i_0\%$ ($4.14 \times 10^{-8} \text{ g} \cdot \text{L}^{-1}$ PFOA)	$\Delta i / i_0\%$ ($4.14 \times 10^{-9} \text{ g} \cdot \text{L}^{-1}$ PFOA)	$\Delta i / i_0\%$ ($4.14 \times 10^{-10} \text{ g} \cdot \text{L}^{-1}$ PFOA)
2	19.4 %	2.0 %	0 %	0%
5	25.6 %	3.9 %	2.1 %	0%
30	37.3%	15.3 %	7.3 %	0%
60	48.5%	24.8 %	15.8 %	10.0%
90	56.8%	35.4 %	22.2 %	15.0%
120	72.1%	47.6 %	31.6 %	18.5%
150	80.0%	56.4 %	40.4 %	30%

180	85.0%	65.4 %	59.7 %	48.3%
210	86.6%	74.1 %	68.9 %	67.5%
240	87.3%	78.5 %	71.5 %	69.1%

182

183 **Table S2.** The decrease in current density of the anodic peak of TEMPO after being exposed to
 184 PFOA in a concentration range of $4.14 \times 10^{-4} \text{ g} \cdot \text{L}^{-1}$ to $4.14 \times 10^{-9} \text{ g} \cdot \text{L}^{-1}$ for 5 minutes.

Concentration ($\text{g} \cdot \text{L}^{-1}$)	$\Delta i = i - i_0$ (μA)
4.14×10^{-4}	25.6 ± 0.8
4.14×10^{-5}	20.7 ± 0.5
4.14×10^{-6}	14.1 ± 1.3
4.14×10^{-7}	9.9 ± 0.8
4.14×10^{-8}	3.9 ± 1.2
4.14×10^{-9}	2.1 ± 0.5

185 i = current density at the anodic peak of TEMPO after exposed to PFOA for 5 minutes, i_0 = current
 186 density at the anodic peak of TEMPO after template removal.

187

188 **Table S3:** Reproducibility of PFOA ($4.14 \times 10^{-9} \text{ g L}^{-1}$) measurements using three PEDOT-
 189 TEMPO-MIP electrodes

MIP electrode	i	i_0	$\Delta i = i - i_0$ (μA)
1	-118.0	-126.4	8.4
2	-115.0	-124.0	9.0
3	-117.7	-127.0	9.3

190 i = current density at the anodic peak of TEMPO after exposed to PFOA for 240 minutes, i_0 = current
 191 density at the anodic peak of TEMPO after template removal.

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198 **Table S4.** The chemical composition of the collected surface water sample.

Analyte	Units	Value
Turbidity	NTU	1.2±0.03
NPOC	mg·L ⁻¹	7.3±0.40
Conductivity	μS·cm ⁻¹	69.9±1.9
Na⁺	mg·L ⁻¹	8.42±0.08
K⁺	mg·L ⁻¹	1.58±0.01
Mg⁺	mg·L ⁻¹	0.95±0.01
Ca⁺	mg·L ⁻¹	2.67±0.03
Cl⁻	mg·L ⁻¹	7.83±0.13
SO₄²⁻	mg·L ⁻¹	0.73±0.10

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