

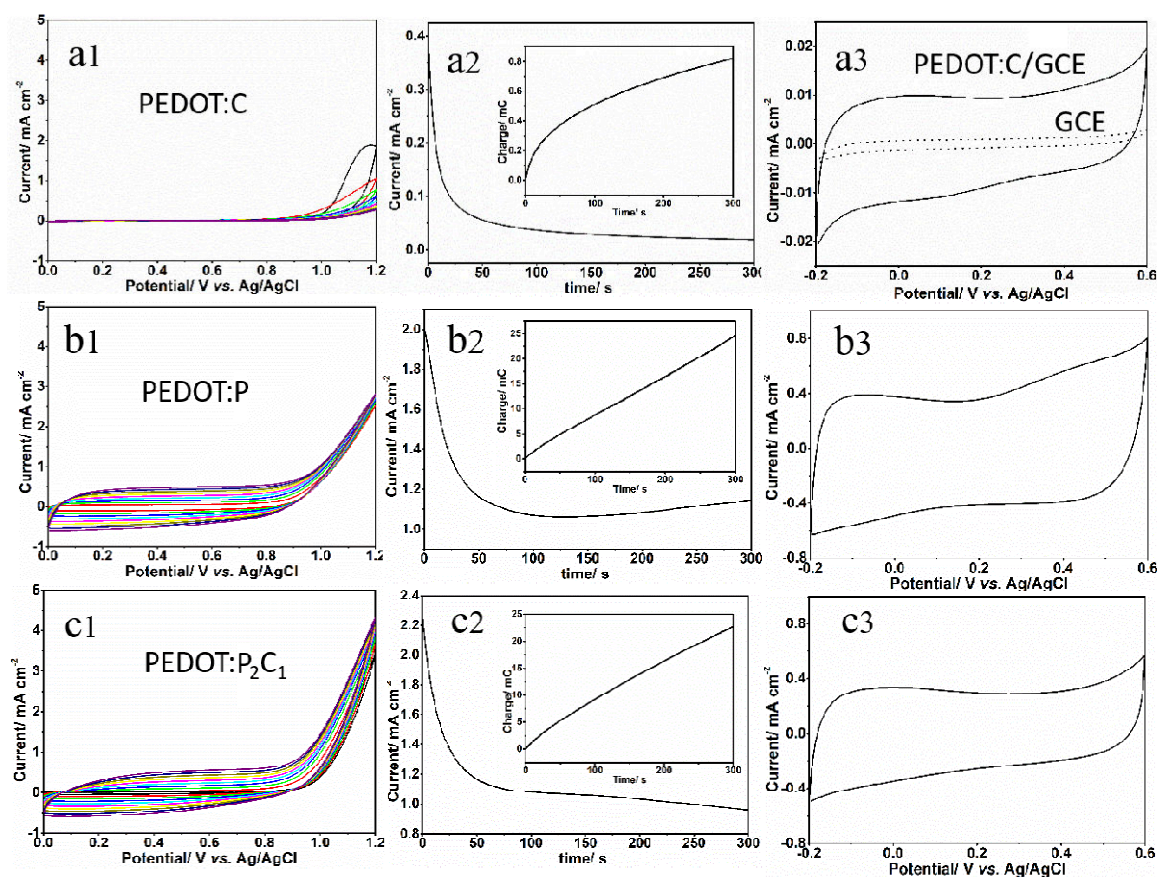
1 **Modulating electrode kinetics for discrimination of dopamine by**
2 **PEDOT:COOH interface doped with negatively-charged tri-carboxylate**

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9 **Figure S1.** Cyclic voltammetry (CVs) and Chronoamperometry (CA) electropolymerization
10 of PEDOT by 10 mM EDOT with 20 mM citrate (a1-2), 20 mM LiClO₄ (b1-2), 10 mM citrate
11 and 20 mM LiClO₄ (c1-2) as dopant and supporting electrolyte; inset of a2, b2 c2 are the
12 corresponding charge of CA electropolymerization. CVs of CA-electropolymerised PEDOT:C

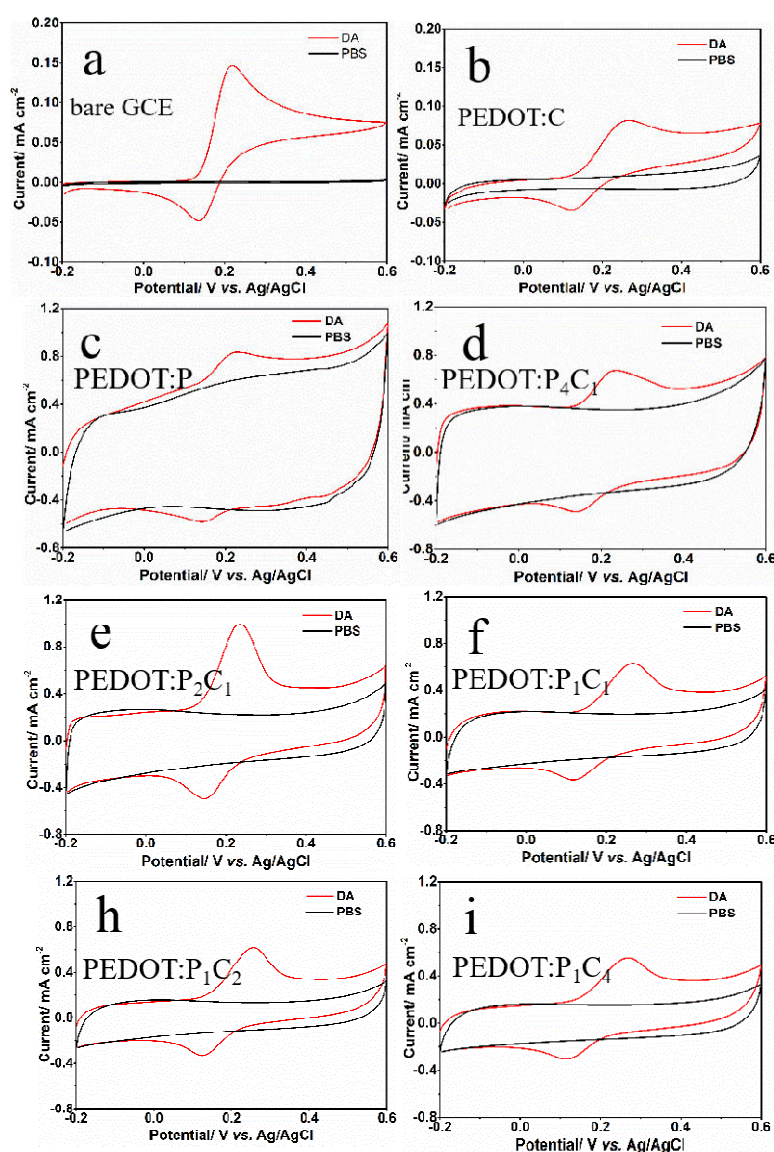
1 (a3), PEDOT:P (b3) and PEDOT:P₂C₁ (c3) in 0.1 M PBS (pH=7.4) with scan rate of 50 mV s⁻¹.
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3 Figure S1 a1 and b1 show the CVs electropolymerization of 10 mM EDOT with 20 mM
4 citrate (a) and LiClO₄ (b) as dopant and supporting electrolyte on GCE. It can be observed from
5 a1 that the onset oxidation potential for EDOT is around 1.0 V, but the current at the range of
6 0-1.0 V demonstrated no apparent increase with the increasing of CV cycles. On the contrary,
7 in the 20 mM LiClO₄ solution, the onset oxidation potential for EDOT decreased to 0.9 V in the
8 first forward scan (b1) and current crossover at about 0.85 V in the reverse scan for beginning
9 of characteristic nucleation process¹. And upon successive cycles, the current showed notable
10 increase, implying successful growth process of PEDOT on the electrode surface.
11 Chronoamperometry (CA) was further used as an alternative technique for PEDOT
12 electropolymerisation at 1.1 V for 300 s and the corresponding current-time curves were shown
13 in a2 and b2. For PEDOT:C, the initial current is ascribed to the charging of double layer,
14 followed by the fast decrease of current to around 0.019 mA cm⁻² with the final deposition
15 charge of 0.86 mC. The initial charging of PEDOT:P is much higher than that of PEDOT:C and
16 decayed more slowly due to the effectively faradaic processes occurring at the electrode surface,
17 with remained current of 1.15 mA cm⁻² at the end. The deposition charge of PEDOT:P (24.55
18 mC) is 28.5 times higher than that of PEDOT:C. The obvious difference between LiClO₄ and
19 citrate may be explained by anion mobility due to the higher doping affinity of ClO₄⁻ as a
20 counterion compared to citrate. During the electropolymerization process, polaron-anion ionic
21 pairs formed and were trapped in the polymer matrix. The more mobile anions (ClO₄⁻) will be
22 replaced by monomer molecules in a faster way than that of slower ones (citrate)¹. Therefore,
23 increasing currents were observed for the following scans with increased amount of PEDOT
24 electropolymerization. The CA-electropolymerised PEDOT:C and PEDOT:P electrodes were
25 also tested in 0.1 M PBS (pH=7.4) by CVs. The PEDOT:C electrode (a3) showed quite small
26 capacitance rectangular box that is slightly higher than bare GCE (dash curve in a3), while
27 PEDOT:P electrode possessed more than 38 times broader background in b3. All the results
28 certified the non-effective electropolymerisation efficiency of PEDOT by citrate on the

1 electrode surface compared to LiClO_4 . Taking 10 mM citrate and 20 mM LiClO_4 as dopant and
2 supporting electrolyte, the CVs and CV electropolymerization showed similar trend to LiClO_4
3 with increased electropolymerization efficiency compared to citrate. The deposition charge of
4 PEDOT:P₂C₁ is 23.60 mC, which is slightly lower than PEDOT:P and 27.4 times higher than
5 PEDOT:C.

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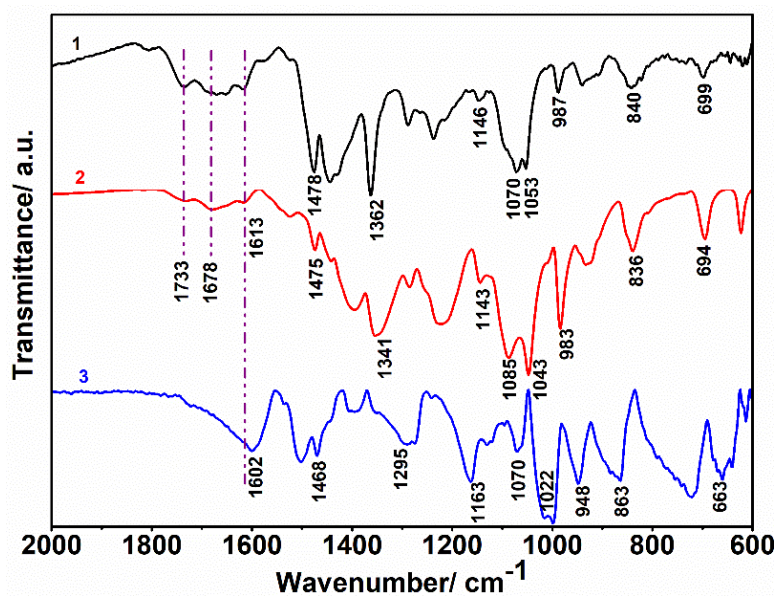
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9 **Figure S2.** CVs bare GCE (a), PEDOT:C (b), PEDOT:P (c), PEDOT:P₄C₁ (d), PEDOT:P₂C₁ (e)
10 PEDOT:P₁C₁ (f), PEDOT:P₁C₂ (h), and PEDOT:P₁C₄ (i), respectively without (black curve) and
11 with 0.5 mM DA in 0.1 M PBS (pH 7.4) with scan rate of 50 mV s⁻¹.

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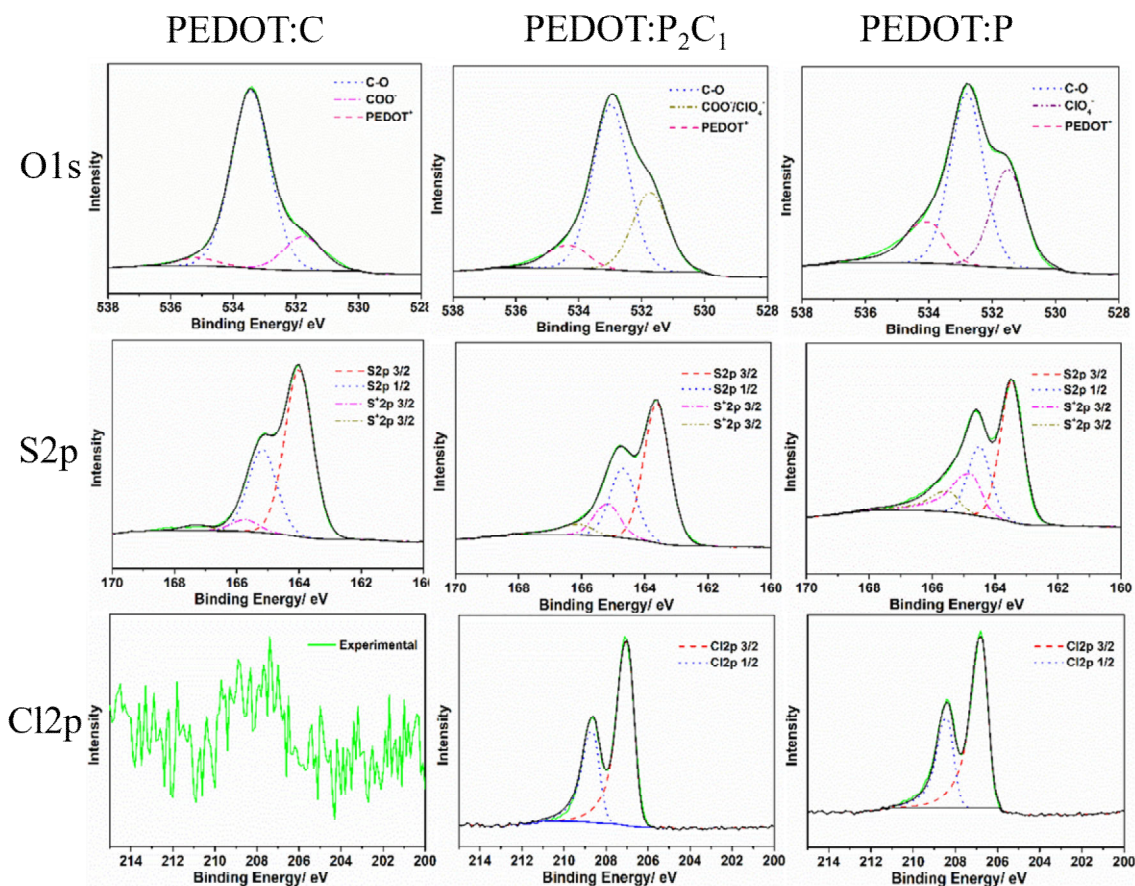
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3 **Figure S3.** FTIR spectra of PEDOT:C (1), PEDOT:P₂C₁ (2) and PEDOT:P (3).

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5 FTIR spectra were used to characterize the doping effect of citrate and LiClO₄ on the
 6 PEDOT films. On the whole, the PEDOT:P₂C₁ spectrum (curve 2) shows the shape similar to
 7 PEDOT:C (curve 2) and shifted peak positions as PEDOT:P (curve 3) spectrum, which may be
 8 caused by the co-doping effect from citrate and ClO₄⁻. As shown in PEDOT:C (curve 1) and
 9 PEDOT:P₂C₁ (curve 2) spectra in the Fig. S3, the bands at bands at 1733 and 1678 cm⁻¹ were
 10 assigned to C=O stretching of the COOH group²⁻⁴, suggesting the successful doping of ternary
 11 citrate into the PEDOT films. The bands at 1613 cm⁻¹ for PEDOT:C and PEDOT:P₂C₁ spectra
 12 are considered to be the characteristic peak of the PEDOT-doped state, while the band at
 13 PEDOT:P spectrum shifted to around 1602 cm⁻¹. For PEDOT:C, the C=C and C-C stretching
 14 in the thiophene moiety appear at 1478 and 1632 cm⁻¹.⁵⁻⁶ The bands at 1146, 1070, 1053 cm⁻¹
 15 are ascribed to the C-O-C stretching in the ethylenedioxy group, while the bands at 987, 840
 16 and 699 are attributed to the C-S bond stretching.⁷ Compared to the PEDOT:C, PEDOT:P₂C₁
 17 demonstrates the same bands with small shift. For the thiophene ring, the C=C and C-C
 18 stretching are located at 1475 and 1431 cm⁻¹, while C-S bond stretching are at 983, 836 and 694
 19 cm⁻¹. And for the ethylenedioxy ring, the C-O-C stretching bands are at 1143, 1085 and 1043
 20 cm⁻¹. The PEDOT:P shows the typically electropolymerized PEDOT spectrum with the C=C

1 and C-C stretching at 1468 and 1295 cm^{-1} , and C-S bond stretching at 948, 863 and 663 cm^{-1} ,
 2 while C-O-C stretching bands at 1163, 1070 and 1022 cm^{-1} .

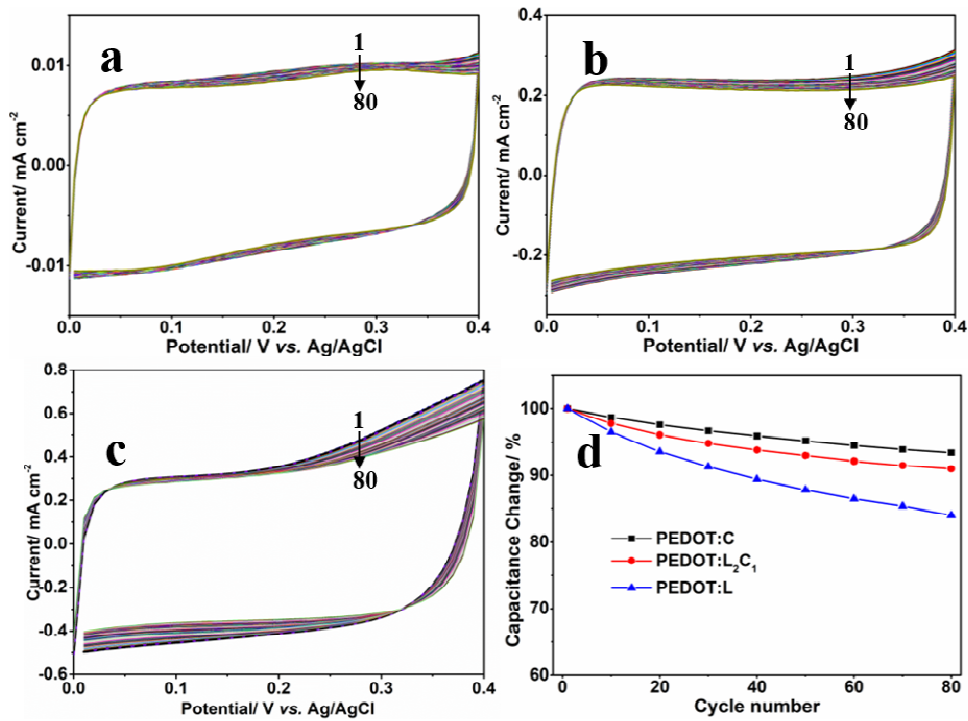


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 4 **Figure S4.** High resolution XPS spectra of O1s, S2p and Cl2p core-level for PEDOT:C,
 5 PEDOT:P and PEDOT:P₂C₁.

6 **O1s:** The characteristic C-O bonding was present as main peaks in PEDOT:C (533.4 eV),
 7 PEDOT:P₂C₁ (533.0 eV) and PEDOT:P (532.7 eV). The smaller peaks at 535.2 eV (PEDOT:C),
 8 534.3 eV (PEDOT:P₂C₁) and 534.0 eV (PEDOT:P) are ascribed to the doped state PEDOT⁺.⁸
 9 The peaks at 531.8 in PEDOT:C and 531.5 eV in PEDOT:P are assigned to citrate and ClO₄⁻,
 10 respectively. In PEDOT:P₂C₁, the peak at 531.7 eV can be assigned to the co-contribution of
 11 citrate and ClO₄⁻.

12 **S2P:** The main sulfur spin-split peaks (S2p 3/2 and S2p 3/2) with a separation of 1.1 eV are
 13 assigned for the S in PEDOT ring for all these three PEDOT interfaces⁹⁻¹⁰. The other pair of
 14 doublet peaks at high binding energy originate from the positively charged sulfur in the
 15 thiophene moiety due to the π -electrons delocalization.^{8, 10}

1 **Cl2p:** For PEDOT:C , there is no Cl2p peaks. In PEDOT:P and PEDOT:P₂C₁, the Cl 2p spectra
 2 show the ClO₄⁻ characteristic spin-split peaks with a 1.6 eV separation. And they have an
 3 asymmetric tail to the high binding energy sites because of ClO₄⁻ charging effects by the
 4 positively charged sulfur within the thiophene ring.¹⁰
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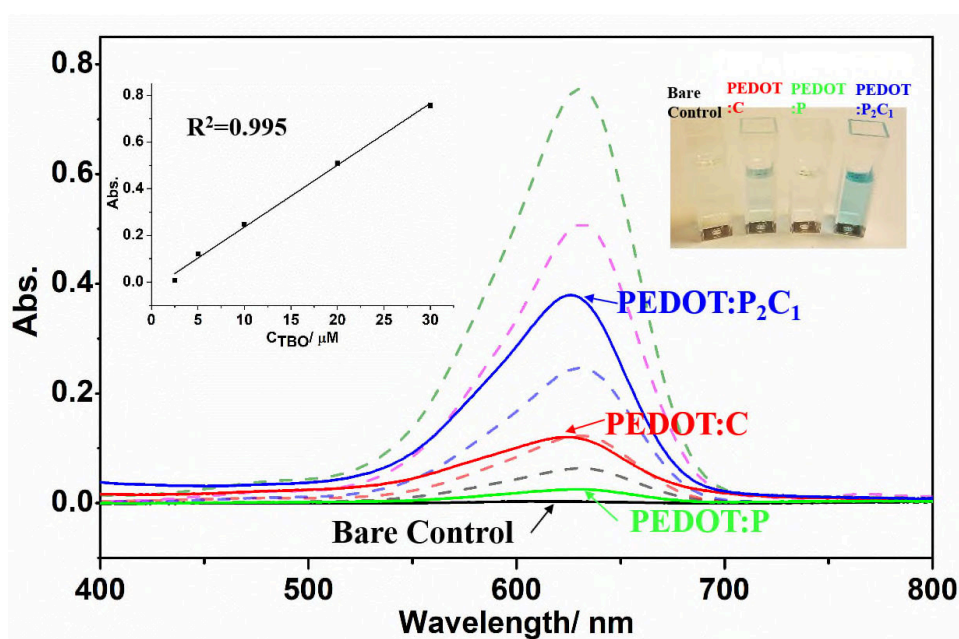


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 7 Figure S5. Stability test from CVs of PEDOT:C (a), PEDOT:P₂C₁ (b) and PEDOT:P (c) in PBS
 8 (0.1 M, pH 7.4) at a scan rate of 50 mV s⁻¹. (d) the capacitance changes of different PEDOT
 9 electrodes quantified by CV curves in the range of 0-0.4 V.

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 11 The stability of the PEDOT-modified electrodes were tested by observing the CVs in PBS
 12 (0.1 M, pH 7.4) over range of 0-0.4 V. As shown in Figure 5S, the PEDOT:C (a), PEDOT:P₂C₁
 13 (b) and PEDOT:P (c) showed slightly decreased current with increase of cycling numbers. The
 14 charge capacitance for different PEDOT electrodes was calculated from the CVs to evaluate the
 15 stability of PEDOT in Figure 5S d. After 80 cycles, the PEDOT:C electrode remained at 93.4 %
 16 of its initial capacitance value, implying good stability of PEDOT doped with citrate. However,
 17 for the PEDOT:P, the capacitance was only able to retain 84.0 % of the initial value. That can
 18 be ascribed to the gradual leakage of ClO₄⁻ from PEDOT matrix. Compared to that of PEDOT:P,

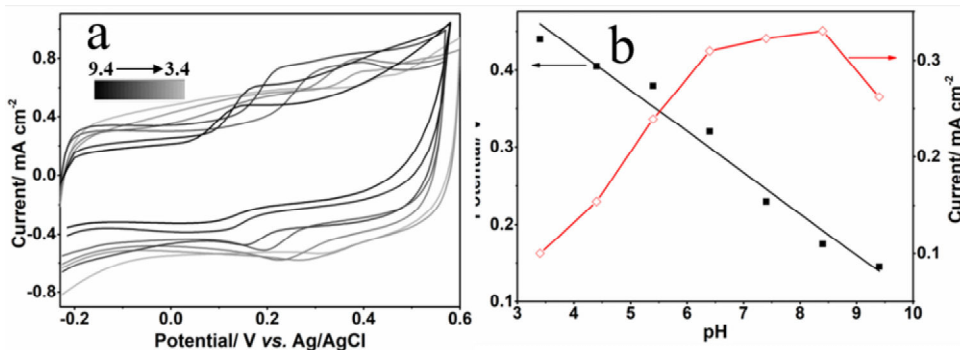
1 the PEDOT:P₂C₁ electrodes showed improved stability with 91.0 % of its initial value
2 remaining. The increased cycling stability and decreased leakage of dopant (citrate) from the
3 PEDOT matrix may be caused by the higher doping stability due to the tri-carboxylic acid
4 groups compared to the small dopant ClO₄⁻.

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9 **Figure S6.** Absorbance spectra of TBO standard solution from 2.5-30 μM (dash line) and
10 dissolved dye solution for bare substrate control, PEDOT:C, PEDOT:P and PEDOT:P₂C₁
11 electrodes, left inset is the corresponding calibration curve for TBO concentration vs.
12 Absorbance (Regression equation: $A = 0.02652C - 0.03056$, $R^2 = 0.995$), right inset is the digital
13 photos of dissolved dye solution for different PEDOT electrodes.

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 2 **Figure S7.** (a) CVs response of 0.5 mM DA at PEDOT:P interface in 0.1 M PBS with various
 3 pH ranging 3.4-9.4; (b) (d) corresponding plots of peak potential and current density vs pH.
 4 Scan rate 50 mV s⁻¹.

5 The peak potential shifted negatively with the pH increase, indicating that the
 6 electroactivity of DA is pH dependent. And the oxidation peak potentials towards DA at the
 7 PEDOT:P were linearly proportional to pH according to the equation: $E_{pa} = 0.641 - 0.053 \text{ pH}$ (R^2
 8 = 0.969). The slope of -0.053 V/pH is close to the theoretical value of -0.059 V/pH. The
 9 oxidation current density increased gradually with increase of pH, and reached the highest peak
 10 current density at 8.4, then decreased after 8.4.

Table S1. Fitted parameters obtained by EIS spectra of PEDOT:P2C1 and PEDOT:P in 0.1 M PBS (pH 7.4) without and with 0.5 mM AA, 0.5 mM DA and 0.5 mM UA at their corresponding oxidation peak potential.

	Potential (V)	System	Rs (Ω)	Rct (k Ω)	Rct change ^a (%)	W (Ω s ^{-1/2})	W change ^b (%)	Q (S s ⁿ)	n
PEDOT:P2C1	0.240	PBS	153	439	66.7	0.0339	142.2	0.383	0.986
		PBS+DA	140	146		0.0821		0.452	0.919
	0.190	PBS	189	524	26.7	0.0503	54.7	0.368	0.971
		PBS+AA	180	384		0.0778		0.359	0.968
	0.350	PBS	151	485	29.3	0.0502	38.4	0.363	0.941
		PBS+UA	145	343		0.0695		0.353	0.938
PEDOT:P	0.240	PBS	182	485	46.4	0.0414	68.8	0.689	0.947
		PBS+DA	177	260		0.0699		0.647	0.892
	0.030	PBS	160	653	76.1	0.0528	51.5	0.470	0.928
		PBS+AA	147	156		0.0800		0.447	0.856
	0.345	PBS	191	497	66.2	0.0433	125	0.625	0.954
		PBS+UA	172	168		0.0975		0.600	0.950

Note: ^aRct Change=[Rct_(PBS) - Rct_(PBS+analyte)]/Rct_(PBS)×100%; ^bW change=[W_(PBS+analyte) - W_(PBS)]/W_(PBS)×100%

Electrochemical impedance spectroscopy (EIS) measurements were carried out at PEDOT electrodes in 0.1 M PBS (pH=7.4) in the presence/absence of different analytes (DA, AA or UA, 0.5 mM) with a frequency range of 0.01 Hz to 100 kHz, 5 mV amplitude, and corresponding oxidation peak potential for different analytes. The impedance spectra were then fitted to an equivalent electrical circuit via ZSimpWin Software (AMETEK Scientific instruments), in which R_s is the solution resistance, R_{CT} is charge transfer resistance as a measure of electrode reaction kinetics, W is generalized finite Warburg element corresponding to the diffusion contribution, Q is the constant phase element, n is the fitted exponent factor.¹¹⁻¹⁴

Table S2. Comparison of the determination of DA at various PEDOT modified electrodes

Electrode	Technique	Linear range (μM)	Sensitivity ($\mu\text{A } \mu\text{M}^{-1}$)	Detection limit (μM)	Reference
PEDOT/CNT/CPE	DPV	0.1-20	-	0.02	Xu ¹⁵
PEDOT/ionic liquid/GCE	Amperometry	0.2-312	0.04535	0.051	Ge ¹⁶
PEDOT/Pd/GCE	DPV	0.5-1	1.9	0.5	Harish ¹⁷
PEDOT/Pd/rGO/GCE	DPV	1-200	0.0213	0.14	Choe ¹⁸
PEDOT/Ni/Si/MCP	DPV	12-48	0.0054 ($\mu\text{A cm}^{-2} \mu\text{M}^{-1}$)	1.5	Yu ¹⁹
PEDOT/NF/CD/Au	DPV	2-320	0.1191	0.003	Atta ²⁰
PEDOT/SDS/Pt	LSV	0.5-25, 30-100	-	0.061, 0.086	Atta ²¹
PEDOT:P/GCE	DPV	5-85	0.0550 ($0.778 \mu\text{A cm}^{-2} \text{mM}^{-1}$)	1.25	This work
PEDOT:P ₂ C ₁ /GCE	DPV	1-85	0.228 ($0.00324 \mu\text{A cm}^{-2} \mu\text{M}^{-1}$)	0.15	This work

Note. CNT: carbon nanotube; CPE: carbon paste electrode; MCP: microchannel plate; NF: Nafion; CD: β -cyclodextrin; SDS: sodium dodecyl sulfate.

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