

## Supporting Information

for

### Chemically synthesized poly(3,4-ethylenedioxythiophene) conducting polymer as a robust electrocatalyst for highly efficient dye-sensitized solar cells

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## **Materials**

All reagents, and anhydrous solvents were purchased from either TCI, Alpha, Sumchun, or Aldrich and used as received without further purification. Cobalt complexes and SGT-021 porphyrin dye were synthesized according to previous reports.<sup>1,2</sup>

## **Experimental Section**

### **Synthesis of PEDOT by oxidative polymerization without surfactant**

2 Equivalent of ammonium persulfate (APS) (13.692 g, 0.06 mol) was dissolved in 200 mL water at 250 mL Schlenk flask. 1 equivalent (3.18 mL, 0.03 mol) of EDOT was added dropwise under an inert atmosphere. The resulting solution was stirred for 72 hours at room temperature (25 °C). The color of the solution mixture is changed from green through blue to dark blue. The obtained dark blue precipitation was collected through filtration and washed with excess water to remove oxidants. The product was finally washed with 20/3 methanol/acetone (v/v) mixed solvents to remove unreacted monomers. The PEDOT polymer was air-dried, followed by vacuum-dried at room temperature. The obtained yield was 80%.

### **Synthesis of PEDOT by oxidative polymerization with surfactant**

To see the effect of surfactant on PEDOT polymerization, sodium dodecylsulfate (SDS) was used. 0.14 g Sodium dodecylsulfate (SDS) (2.5 mM) was added in 200 mL water in 250 mL Schlenk flask and stirred for 1 h. 2 Equivalent of ammonium persulfate (APS) (13.692 g, 0.06 mol) or 2.4 equivalent of FeCl<sub>3</sub> was added in the SDS solution and stirred for 1 h. The solution was degassed with Ar-gas for 30 min. 1 equivalent (3.18 mL, 0.03 mol) of EDOT was added dropwise under an inert atmosphere. The resulting solution was stirred for 72 hours at room

temperature (25 °C). The color of the solution mixture is changed from green through blue to dark blue. The obtained dark blue precipitation was collected through filtration and washed with excess water to remove oxidants. The product was finally washed with 20/3 methanol/acetone (v/v) mixed solvents to remove unreacted monomers. The PEDOT polymer was air-dried, followed by vacuum-dried at room temperature. The obtained yield was 31% for the APS oxidant and 26% for FeCl<sub>3</sub> oxidant.

### **Characterization of conducting polymers**

The C, H, and S elemental analysis was performed by an elemental analyzer (Flash 2000). The Fourier transform infrared (FT-IR) spectra of PEDOT nanomaterials were performed by FT/IR (Jasco 4200) spectrophotometer using PEDOT nanomaterial in the KBr pellet. The UV-vis-NIR absorption of PEDOTs was checked by a UV/VIS spectrophotometer (PerkinElmer Lambda 750S). The PEDOT powder sample (5 mg/mL) was dispersed in DMSO using a sonicator and magnetic stirring. The solution was then filtered with 1µm PTFE (Whatman) syringe filter and diluted with DMSO. 1 cm quartz cell was used to measure UV-vis-NIR absorption. The morphology of PEDOTs nanomaterials and spin-coated PEDOTs on FTO substrate was performed by high-resolution FE-SEM (HITACHI S-4800). A thin layer of Pt- was deposited above PEDOT nanomaterials which are placed on adhesive tape in the sample holder. In the case of spin-coated PEDOT film on the FTO substrate, no-addition Pt-coating was performed for SEM analysis. X-ray diffraction (XRD) patterns of PEDOT nanomaterials were performed by Smartlab X-ray diffractometer (Rigaku) at 30kV and 30 mA. A Micromeritics ASAP 2020 plus was used to obtain the N<sub>2</sub> adsorption/desorption isotherm. Free space correction was measured in ultra-high purity (UHP) helium gas (99.999 % purity). The N<sub>2</sub> isotherm was measured at 77 K.

N<sub>2</sub> adsorption/desorption measurements were conducted at 77 K after activation at 50 °C for 2 days under dynamic vacuum at 5 μmHg.

The weight loss of PEDOT nanomaterials with temperature under air-oxidizer was performed by the thermogravimetric analyzer (Scinco TGA N-1000) at 10 °C min<sup>-1</sup>. The sheet resistance (Ω/Sq) was checked by automated 4 probe sheet resistance measurement (CMT-Series, Advanced Instrument Technology) by PEDOT pellet with a thickness of 300-800 nm. Then electrical conductivity was estimated from sheet resistance by multiplying the thickness of the pellet.

**Table S1** Elemental analysis of synthesized PEDOTs and estimation of SO<sub>4</sub><sup>2-</sup> dopant ratio

	Elemental distribution	Total	(-C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> S-) <sub>n</sub> <sup>a</sup>	SO <sub>4</sub> <sup>2-</sup>	unaccounted
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		Experimental		(dopant)	
<b>PEDOT-1</b>	C (mass%)	45.3	45.3		-
	H (mass%)	3.1	2.5		0.6
	S (mass %)	22.2	20.1	2.1	-
	O (mass %)	-	20.1	4.2	-
	Total mass in 100g	70.6	88	6.3	
	Molar mass (gmol <sup>-1</sup> )		140 <sup>b</sup>	96	
	Amount (mol) in 100g		0.63	0.066	
	<b>Mole ratio of SO<sub>4</sub><sup>2-</sup></b>			<b>0.10</b>	
<b>PEDOT-2</b>	C (mass%)	44.8	44.8		-
	H (mass%)	3.0	2.5		0.5
	S (mass %)	21.5	19.9	1.6	-
	O (mass %)	-	19.9	3.2	-
	Total mass in 100g	69.3	87.1	4.8	
	Molar mass (gmol <sup>-1</sup> )		140 <sup>b</sup>	96	
	Amount (mol) in 100g		0.62	0.049	
	<b>Mole ratio of SO<sub>4</sub><sup>2-</sup></b>			<b>0.079</b>	
<b>PEDOT-3</b>	C (mass%)	44.9	44.9		
	H (mass%)	3.3	2.5		0.8
	S (mass %)	20.6	19.9	0.6	-
	O (mass %)	-	19.9	1.2	
	Total mass in 100g	68.8	87.2	1.8	
	Molar mass (gmol <sup>-1</sup> )		140 <sup>b</sup>	96	
	Amount (mol) in 100g		0.62	0.019	
	<b>Mole ratio of SO<sub>4</sub><sup>2-</sup></b>			<b>0.031</b>	
<b>PEDOT-4</b>	C (mass%)	43.4	43.4		
	H (mass%)	3.5	2.4		1.1
	S (mass %)	19.0	19.3		
	O (mass %)	-	19.3		
	Total mass in 100g	65.9	84.4		
	Molar mass (gmol <sup>-1</sup> )		140 <sup>b</sup>	-	
	Amount (mol) in 100g		0.60		

<sup>a</sup>PEDOT

<sup>b</sup>For each monomer unit

**Table S2** PEDOT synthesized from aqueous oxidative polymerization of EDOT

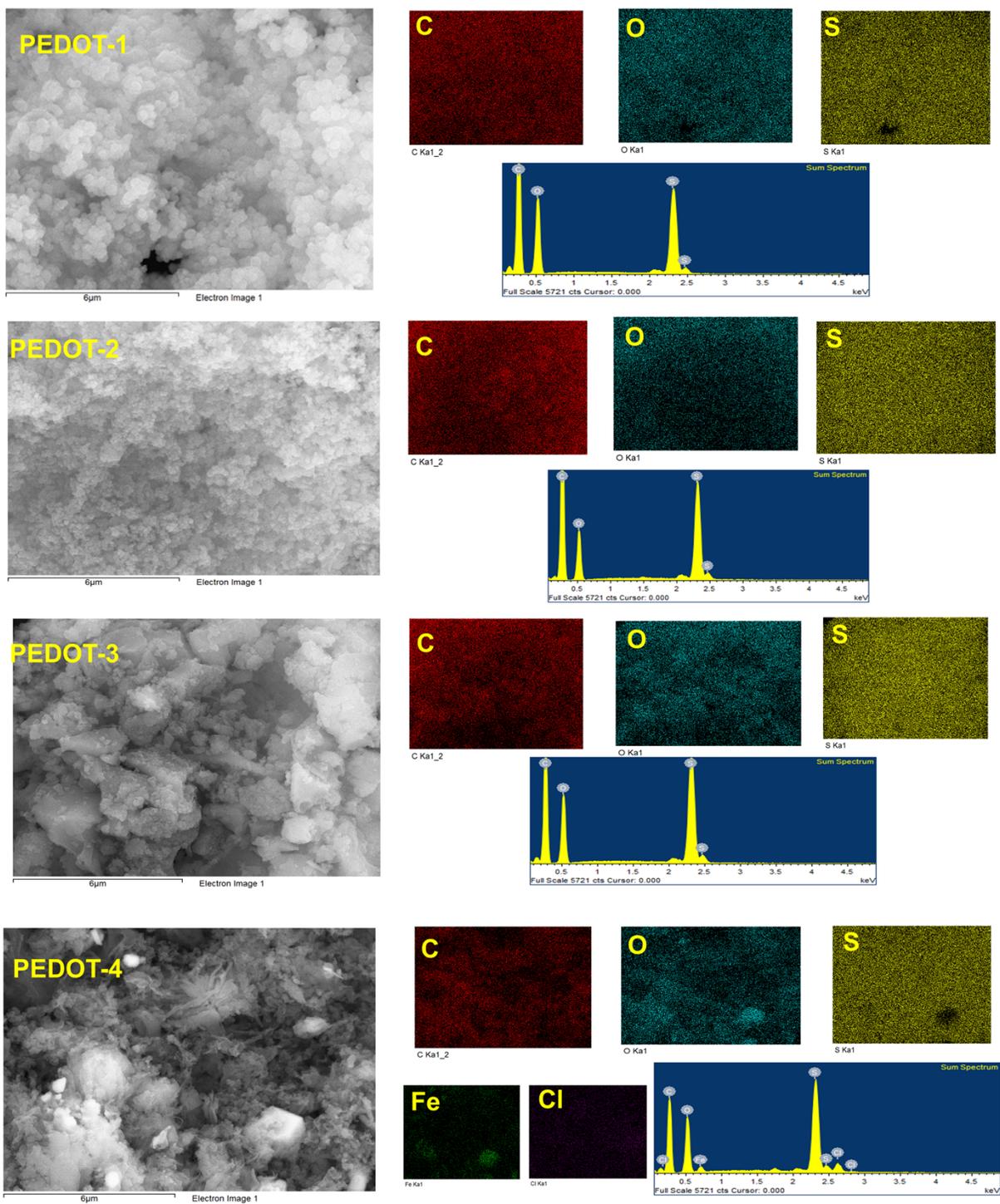
Sample Name	Oxidant (conc.)	EDOT: Oxidant	SDS Conc.	Yield (%)	<sup>a</sup> Dopant % (SO <sub>4</sub> <sup>2-</sup> )	<sup>b</sup> $\sigma$ (S cm <sup>-1</sup> )	<sup>c</sup> Particle size (nm)
PEDOT-1	APS (0.15 M)	1:1	-	65.6	10	5.39 ±0.70	132 ±22.7
PEDOT-2	APS (0.3 M)	1:2	-	79.7	8	3.22 ±0.29	114 ±44.0
PEDOT-3	APS (0.3 M)	1:2	2.5 mM	30.5	3	6.57 ±2.13 x 10 <sup>-5</sup>	400-600 (diameter)
PEDOT-4	FeCl <sub>3</sub> (0.4 M)	1:2.4	2.5 mM	25.8	-	16.42 ±6.82	77 ±15.2 (diameter)

<sup>a</sup>The doping level of PEDOT was estimated from elemental analysis (see **Table S1**). <sup>b</sup>The

intrinsic electrical conductivity was estimated by sheet resistance measurement of PEDOT-pellet

by 4 probe analysis. The pellet was obtained by mechanically pressing PEDOT powder. <sup>c</sup>The

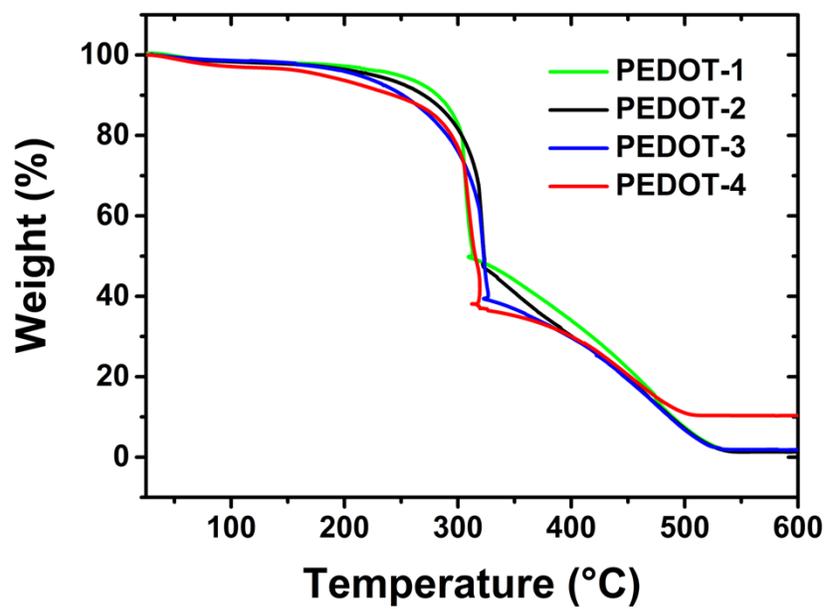
particle size was estimated from SEM-analysis (see **Fig. 1**) of PEDOT nano powder.



**Fig. S1** FE-SEM images and EDS elemental mapping of different PEDOT nanomaterials.

**Table S3** Detailed N<sub>2</sub> adsorption parameters to derive the BET surface area. From top left to right: PEDOT-1, PEDOT-2, PEDOT-3, and PEDOT-4.

<b>Parameter</b>	<b>Range</b>	<b>Parameter</b>	<b>Range</b>
P/P <sub>0</sub>	0.02872–0.10041	P/P <sub>0</sub>	0.02866–0.10013
V (at P/P <sub>0</sub> =0.02872)	4.0532 cm <sup>3</sup> g <sup>-1</sup>	V (at P/P <sub>0</sub> =0.02866)	6.2038 cm <sup>3</sup> g <sup>-1</sup>
V (at P/P <sub>0</sub> =0.10041)	5.1063 cm <sup>3</sup> g <sup>-1</sup>	V (at P/P <sub>0</sub> =0.10013)	7.4646 cm <sup>3</sup> g <sup>-1</sup>
R <sup>2</sup>	0.9999388	R <sup>2</sup>	0.9999359
C	131.059305	C	192.79219
V <sub>m</sub>	4.9046 cm <sup>3</sup> g <sup>-1</sup>	V <sub>m</sub>	7.0580 cm <sup>3</sup> g <sup>-1</sup>
1/(√C+1)	0.08033	1/(√C+1)	0.067182
<b>Parameter</b>	<b>Range</b>	<b>Parameter</b>	<b>Range</b>
P/P <sub>0</sub>	0.01298–0.09005	P/P <sub>0</sub>	0.05283–0.25067
V (at P/P <sub>0</sub> =0.01298)	1.7805 cm <sup>3</sup> g <sup>-1</sup>	V (at P/P <sub>0</sub> =0.05283)	1.6723 cm <sup>3</sup> g <sup>-1</sup>
V (at P/P <sub>0</sub> =0.09005)	2.7932 cm <sup>3</sup> g <sup>-1</sup>	V (at P/P <sub>0</sub> =0.25067)	3.5875 cm <sup>3</sup> g <sup>-1</sup>
R <sup>2</sup>	0.9995372	R <sup>2</sup>	0.9961315
C	120.660594	C	19.502215
V <sub>m</sub>	2.7275 cm <sup>3</sup> g <sup>-1</sup>	V <sub>m</sub>	3.1718 cm <sup>3</sup> g <sup>-1</sup>
1/(√C+1)	0.083441	1/(√C+1)	0.18463



**Fig. S2** TGA-curves of chemically synthesized PEDOTs under air-oxidizer.

### **Fabrication of symmetrical cell and PEDOT-FTO counter electrode by spin-coating**

5 wt% PEDOT was dispersed in DMSO through ultrasonication for 15 min and stirring with a magnetic bar for 1 h. Then obtained dark blue/black solution was spin-coated on the FTO substrate (3000 rpm for 40 seconds; for PEDOT-2 and 3, repeated 2 times). The obtained thin film on the FTO substrate was dried overnight under 70°C in a vacuum oven.

Symmetrical cells were fabricated by sandwiching two spin-coated PEDOT counter electrodes using a hot-pressed 30 µm surlyn spacer. The cobalt redox electrolyte was injected through a predrilled hole by backfilling and sealed with surlyn and covered glass with the aid of heat. The composition of the cobalt electrolytes was 0.22 M [Co<sup>2+</sup>(bpy)<sub>3</sub>](TFSI)<sub>2</sub>, 0.05 M [Co<sup>3+</sup>(bpy)<sub>3</sub>](TFSI)<sub>3</sub>, 0.1 M LiTFSI and 0.8 M TBP in acetonitrile.

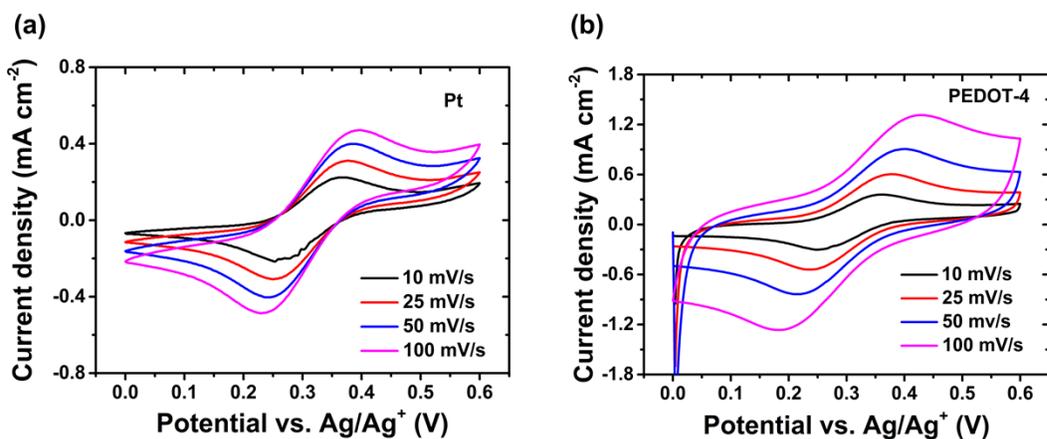
For comparison, the Pt-counter electrode was also fabricated as a reference electrode by drop casting chloroplatinic solution in ethanol on FTO-substrate and then dried at 450 °C for 15 minutes. Pt-symmetrical cells were fabricated similarly to PEDOT symmetrical cells.

### **Fabrication of DSSC**

DSSC was fabricated by sandwiching Pt or PEDOT counter electrode and SGT-021-dye sensitized TiO<sub>2</sub> photoanode using a hot-pressed 30 µm surlyn spacer. The cobalt electrolyte was injected through a pre-drilled hole by backfilling and sealed by cover-glass and surlyn spacer by heat. The TiO<sub>2</sub>-film (~8 µm) on FTO was prepared by screen-printing using commercial 30 NR-D TiO<sub>2</sub> paste (Greatcell Solar Materials) as active layer (~4 µm) and WER2-O reflector TiO<sub>2</sub>-paste (Greatcell Solar Materials) as scattering layer (~4 µm). The TiO<sub>2</sub> film on FTO was then immersed in SGT-021 dye solution for 3 hours at room temperature followed by washing with ethanol. The SGT-021-dye solution was prepared by 0.2 mM SGT-021 and 0.6 mM HC-A1 (co-adsorbent) in THF/ethanol (1/2, v/v) mixed solvent.

## Electrochemical and Photovoltaic Characterization

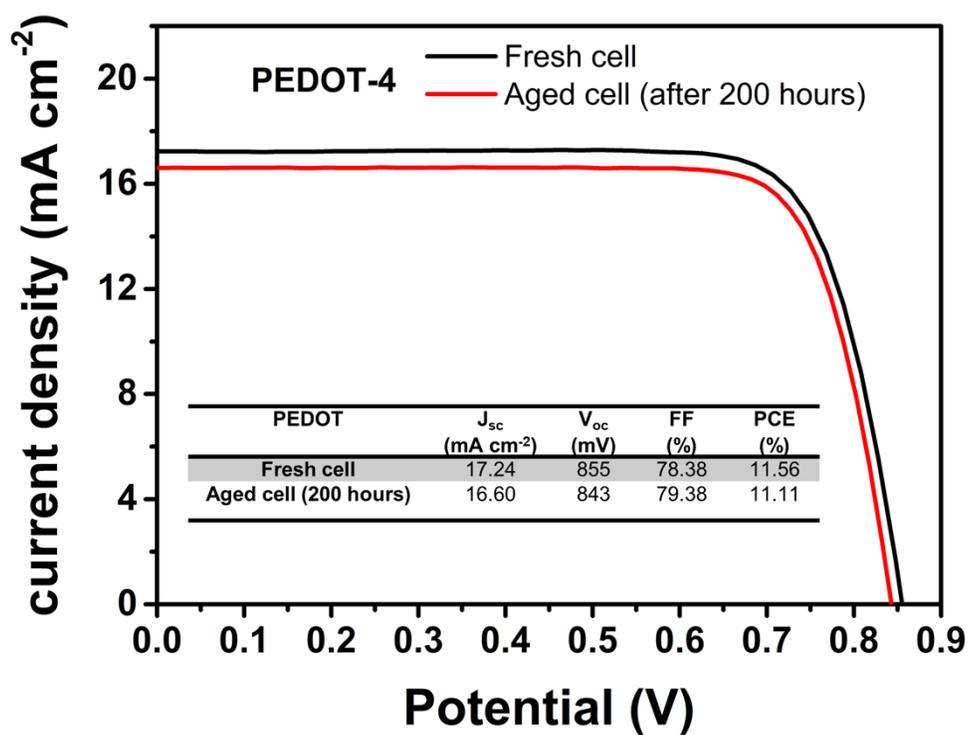
The electrochemical impedance spectroscopy (EIS) of symmetrical cells was measured by potentiostat (VersaSTAT 3, AMETAK) at 0 V in open circuit conditions with a frequency range of  $10^6$ -0.1 Hz and 10 mV (RMS) amplitude. The liner scan voltammetry (LSV) of symmetrical cells was recorded by potentiostat (VersaSTAT 3, AMETAK) from -1V to 1V potential range at 50 mV sec<sup>-1</sup> scan rate. The cyclic voltammogram (CV) of the counter electrode was analyzed by an Iviumstat electrochemical workstation at various scan rates, 10-100 mV s<sup>-1</sup>, and a potential range of 0 to 0.6 V using three electrodes system, where Ag/AgCl, Pt-wire act as reference electrode and counter electrode respectively. Drop-cast Pt-or spin-coated PEDOT on FTO substrate was used as a working electrode. The electrolytes solution for CV analysis was prepared by diluting cobalt electrolytes 100 times (0.5 mL electrolytes in 50 mL acetonitrile) with an additional 0.1 M LiClO<sub>3</sub> salt. The photovoltaic performance of DSSC was evaluated under simulated 1-sun (Standard AM 1.5G, 100 mW cm<sup>-2</sup> from 450 W Xenon lamp) illumination using a solar simulator (Newport Oriel Sol3A class, model 94023A). The light intensity was cross-checked with NREL calibrated silicon reference cell (PV Measurements, Inc.). A black metal mask with an aperture area of 0.141 cm<sup>2</sup> was used for J-V measurement. The EIS of DSSCs was measured in the frequency range of  $10^6$ -0.1 Hz and 10 mv (RMS) amplitude under dark conditions and room temperature at -0.85 V using VersaSTAT3 potentiostat. The induced photo-to-current conversion efficiency (IPCE) was obtained by the QEXL solar cell quantum efficiency measurement system (PV Measurements, Inc.).



**Fig. S3** Cyclic voltammograms of (a) Pt and (b) PEDOT-4 counter electrode at various scan rates.

**Table S4** Cathodic peak current density ( $I_{pc}$ ) and peak-to-peak separation ( $\Delta E_{pp}$ ) for different counter electrodes.

Scan rate (mV/s)	Pt		PEDOT-4	
	$I_{pc}$ (mA cm <sup>-2</sup> )	$\Delta E_{pp}$ (V)	$I_{pc}$ (mA cm <sup>-2</sup> )	$\Delta E_{pp}$ (V)
10	-0.22	0.11	-0.31	0.11
25	-0.31	0.13	-0.54	0.14
50	-0.40	0.14	-0.84	0.18
100	-0.49	0.16	-1.27	0.24



**Fig. S4** Comparison of J-V curves of fresh and aged cells measured under 1 sun conditions.

## References

- 1 Masud, H. Zhou and H. K. Kim, *Mater. Today Energy*, 2023, **34**, 101299.
- 2 S. H. Kang, M. J. Jeong, Y. K. Eom, I. T. Choi, S. M. Kwon, Y. Yoo, J. Kim, J. Kwon, J. H. Park and H. K. Kim, *Adv. Energy Mater.*, 2017, **7**, 1602117.