

Supplementary Information

**Multifunctional conjugated molecules combined with electrospun  
CuCoP/carbon nanofibers as a modifier of Pt counter electrode for dye-  
sensitized solar cells**

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## Materials

### The part of DPPTPTA/CuCoP/CNF

3-(4-Bromophenyl)propionic acid ( $\text{BrC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , 98%), anhydrous diethyl ether ( $\geq 99\%$ ), lithium aluminum hydride (LAH, 95%), hydrochloric acid (HCl, 37%), bis(pinacolato)diboron ( $\text{C}_{12}\text{H}_{24}\text{B}_2\text{O}_4$ , 99%), sodium acetate ( $\text{CH}_3\text{COONa}$ ,  $\geq 99\%$ ), anhydrous 1,4-dioxane (99.8%),  $\text{PdCl}_2(\text{PPh}_3)_2$  ( $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$ , 98%), 1,3,5-tribromobenzene ( $\text{C}_6\text{H}_3\text{Br}_3$ , 98%), anhydrous toluene (99.8%), anhydrous ethanol ( $\geq 99.5\%$ ),  $\text{Pd}(\text{PPh}_3)_4$  ( $\text{Pd}[(\text{C}_6\text{H}_5)_3\text{P}]_4$ , 99.99%), potassium carbonate ( $\text{K}_2\text{CO}_3$ , 99%), 3,6-bis(5-bromothien-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione ( $\text{C}_{46}\text{H}_{70}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2$ , 98%), tetrakis(triphenylphosphine)palladium(0) ( $\text{Pd}(\text{P}(\text{C}_6\text{H}_5)_3)_4$ , 99.99%), anhydrous tetrahydrofuran (THF, 99.9%), 2-azido-1,3-dimethylimidazolium hexafluorophosphate ( $\text{C}_5\text{H}_{10}\text{F}_6\text{N}_5\text{P}$ , 97%), 1,8-diazabicyclo[5.4.0]undec-7-ene ( $\text{C}_9\text{H}_{16}\text{N}_2$ , 98%), polyacrylonitrile (PAN,  $M_w=150,000$ ), dimethylformamide (DMF, 99%), copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ), cobalt(II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 98%) and red phosphorous ( $\geq 99.99\%$ ) were received from Merck Industrial and Lab Chemicals.

### The part of photoanode preparation

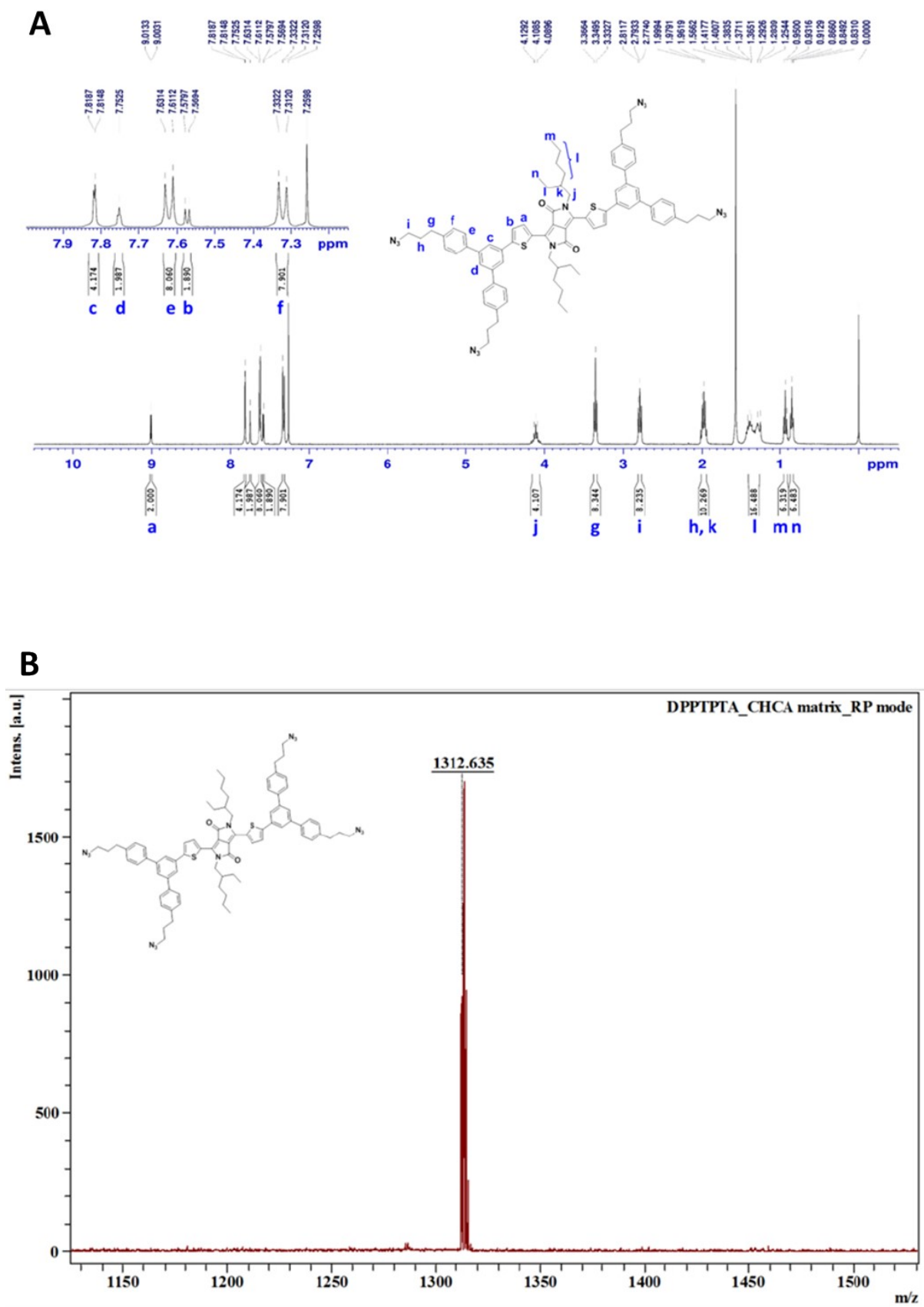
Lithium perchlorate ( $\text{LiClO}_4$ ,  $\geq 98.0\%$ ), titanium(IV) tetraisopropoxide (TTIP,  $>98\%$ ), 2-methoxyethanol (99.95%) were obtained from Sigma-Aldrich. Lithium iodide (LiI, synthetic grade), poly(ethylene glycol) (PEG,  $M_w=20,000$ ) and iodine ( $\text{I}_2$ , synthetic grade) were received from Merck Industrial and Lab Chemicals. 4-tert-butylpyridine (*t*BP, 96%) and tert-butyl alcohol (*t*BA, 96%) were procured from Acros. 3-Methoxypropionitrile (MPN, 99%) and acetonitrile (ACN, 99.99%) were bought from Fluka. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII), Surlyn<sup>®</sup> (SX1170-25, 25  $\mu\text{m}$ ) film, transparent  $\text{TiO}_2$  paste (TL paste, Ti-nanoxide T/SP, with an average particle size = 13 nm), and cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719 dye) were received from Solaronix (S.A., Aubonne, Switzerland). Fluorine-doped tin oxide (FTO) conducting glasses ( $7 \Omega \text{ sq}^{-1}$ , UR-ITO007-0.7 mm) were obtained from NSG America, Inc., New

Jersey, USA. The commercial light scattering TiO<sub>2</sub> particles (ST-41; average particle size = 200 nm) were acquired from Ishihara Sangyo, Ltd.

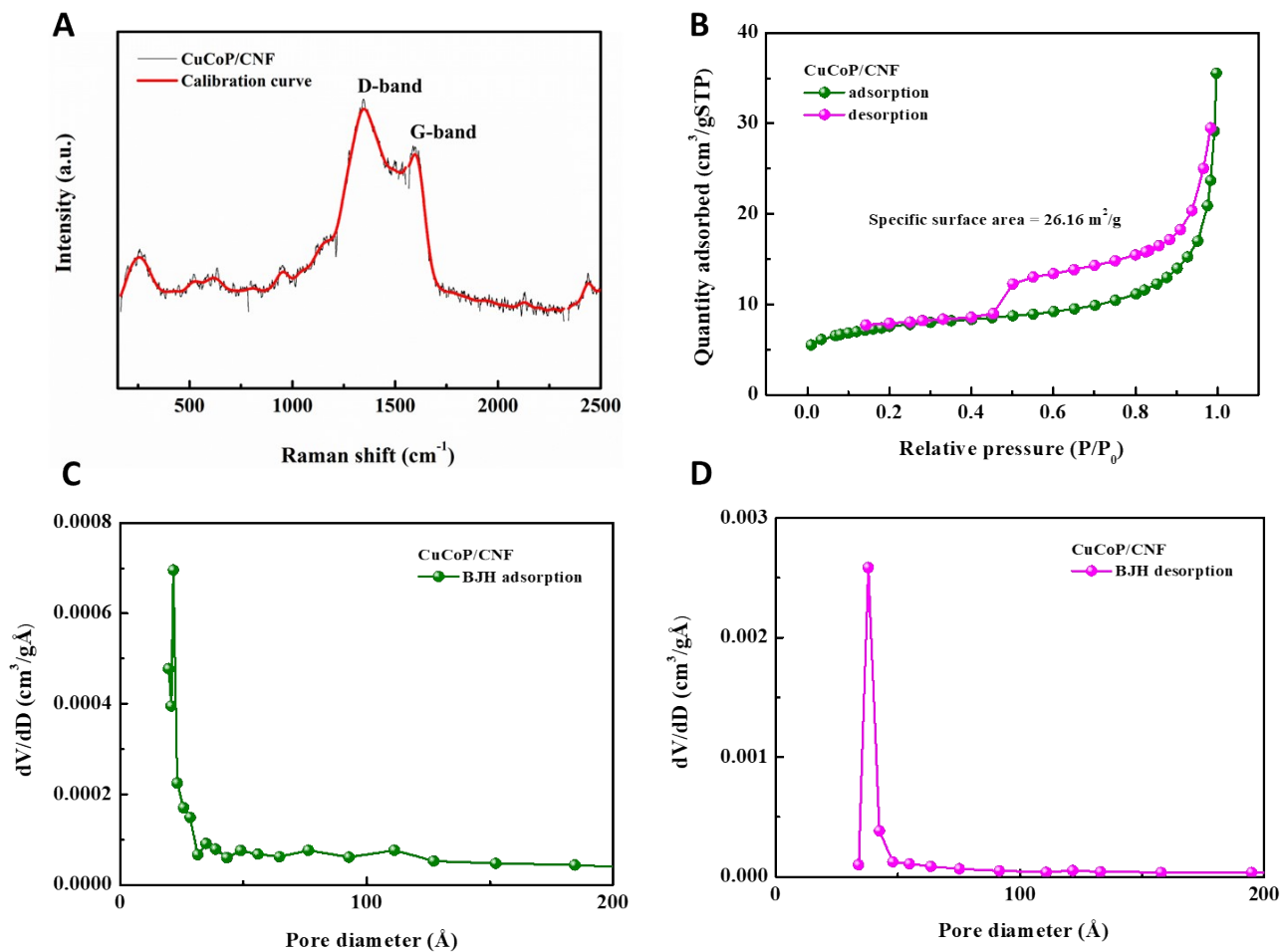
### Cell Assembly

The TiO<sub>2</sub> (100 nm) paste (TTIP in 2-methoxyethanol (weight ratio = 1/3)) was coated on cleaned FTO glasses as the thin compact layers including transparent layer (10 μm) and scattering layer (4 μm) with an active area of 0.196 cm<sup>2</sup> by using the doctor blade technique. Herein, the commercial transparent paste (Ti-nanoxide T/SP) was used to prepare the transparent layer, while a home-made scattering paste was further used to prepare the scattering layer. Each layer was separately sintered at 500 °C for 30 min in ambient environment. After the sintering process, the TiO<sub>2</sub> film was immersed in N719 dye solution (5×10<sup>-4</sup> M of N719 in *t*BA and ACN (volume ratio = 1/1) solvent) for 24 h at room temperature. Finally, the dye-adsorbed TiO<sub>2</sub> photoanode was coupled to PtCE (the Pt layer thickness is around 197.36 μm and area = 3.125 cm<sup>2</sup>) with a modified layer coating, and a cell gap of 25 μm thick Surlyn<sup>®</sup> film as the spacer. The iodide/triiodide electrolyte (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) was prepared by mixing of 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M DMPII and 0.5 M *t*BP in ACN/MPN (volume ratio = 8/2). The iodide/triiodide electrolyte electrolyte was injected into the cell gap between the two electrodes by capillarity to form a device (i.e., photoanode/electrolyte/modified layer/PtCE).

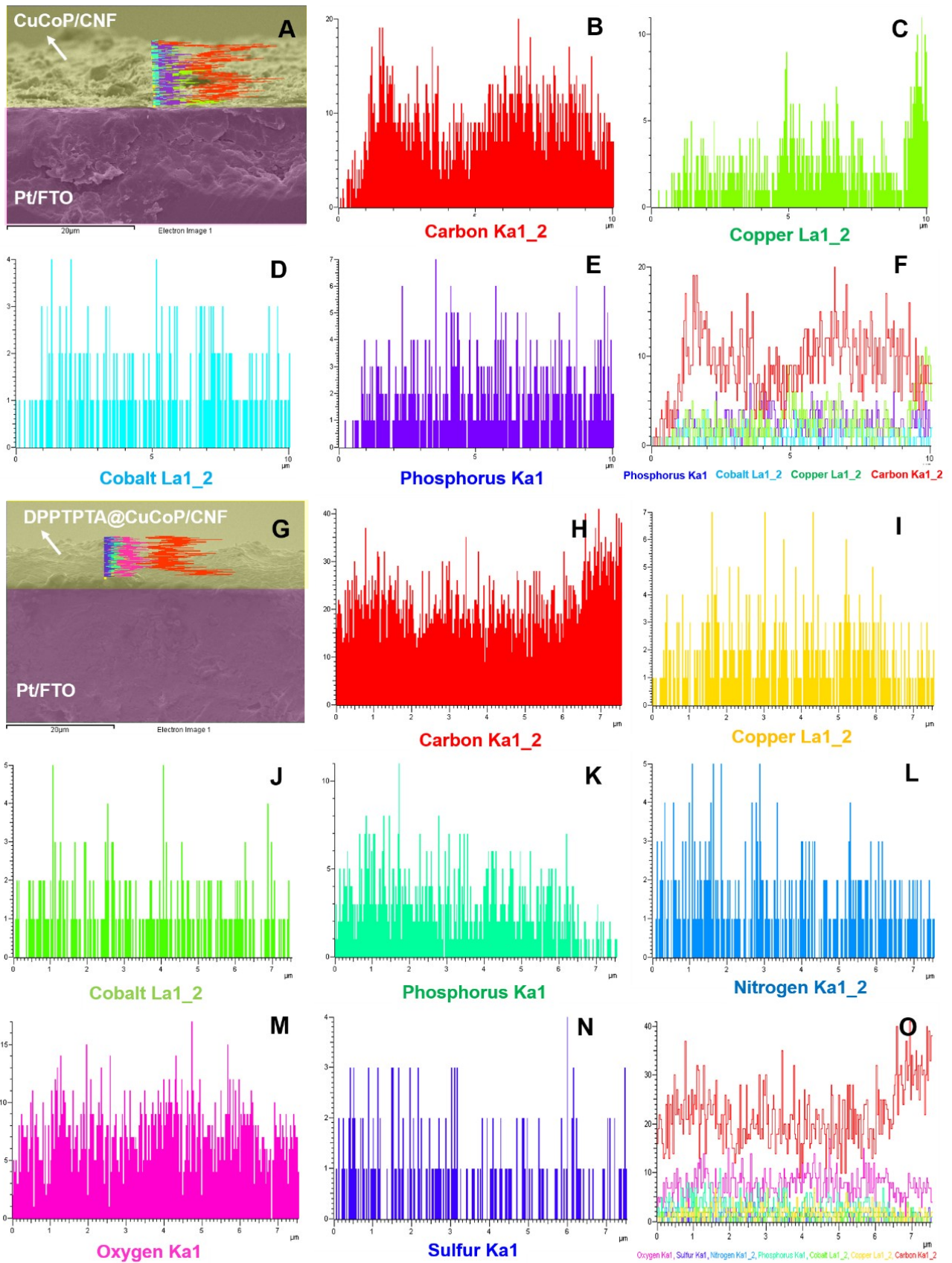
The following three-step process was carried out to prepare the above-mentioned scattering paste: (1) The TiO<sub>2</sub> colloid was synthesized by mixing of 0.5 M TTIP solution with 0.1 M nitric acid aqueous solution and the mixed solution was further stirred at 88 °C for 8 h. (2) The solution was then transferred into an autoclave (PARR 4540, USA) and maintained at 240 °C for 12 h. The TiO<sub>2</sub> nanoparticles could reach an average diameter of 20 nm at this stage. (3) The scattering layer paste was acquired by the addition of 25 wt% PEG and 100 wt% of commercial scattering TiO<sub>2</sub> particles (ST-41) (both with respect to the weight of TiO<sub>2</sub>). In this case, PEG was used for not only preventing the aggregation of TiO<sub>2</sub> nanoparticles, but controlling the pore sizes on the TiO<sub>2</sub> nanoparticles as well.



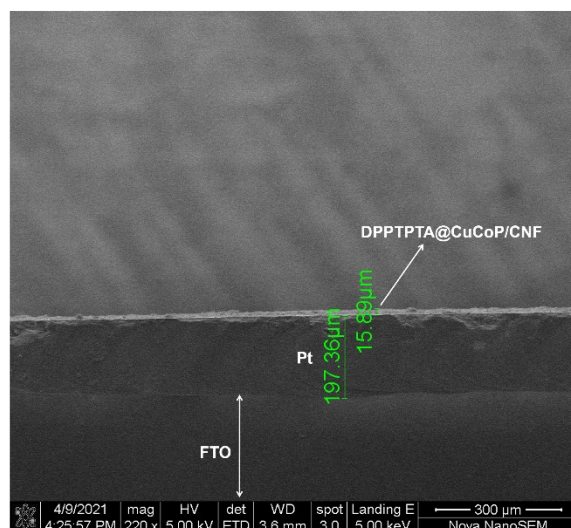
**Fig. S1** (A) FT-NMR spectrum of DPPTPTA, and (B) MALDI-TOF mass spectrum results.



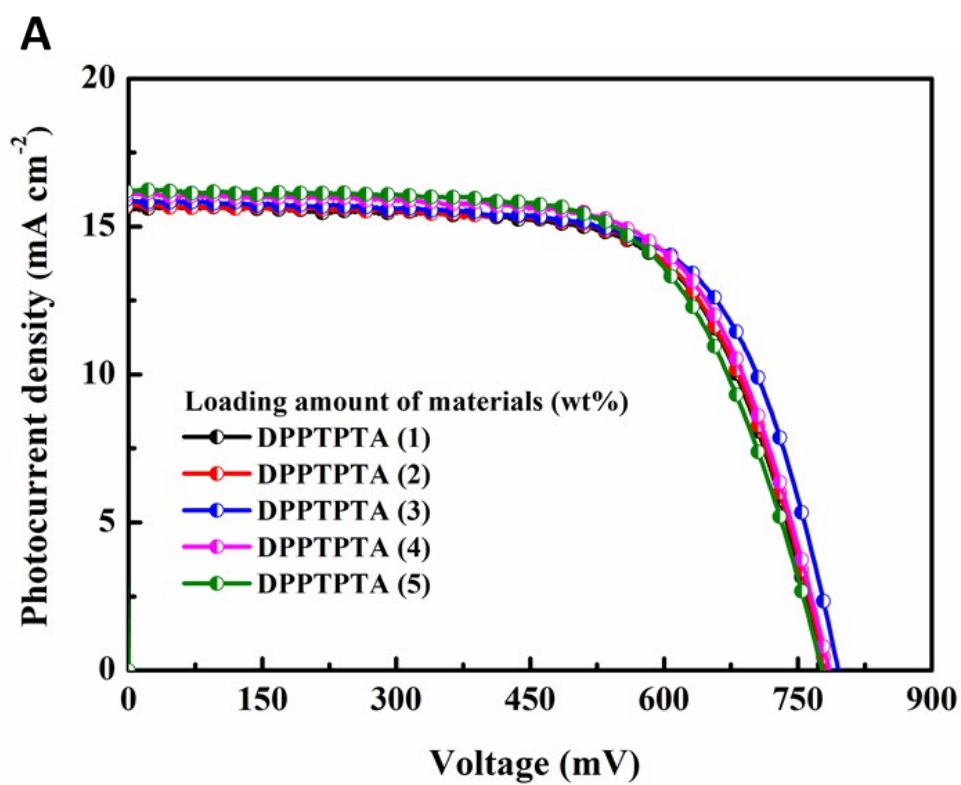
**Fig. S2** (A) In-situ Raman spectroscopy, (B) nitrogen adsorption/desorption isotherm, (C) BJH adsorption curve and (D) BJH desorption curve of CuCoP/CNF.

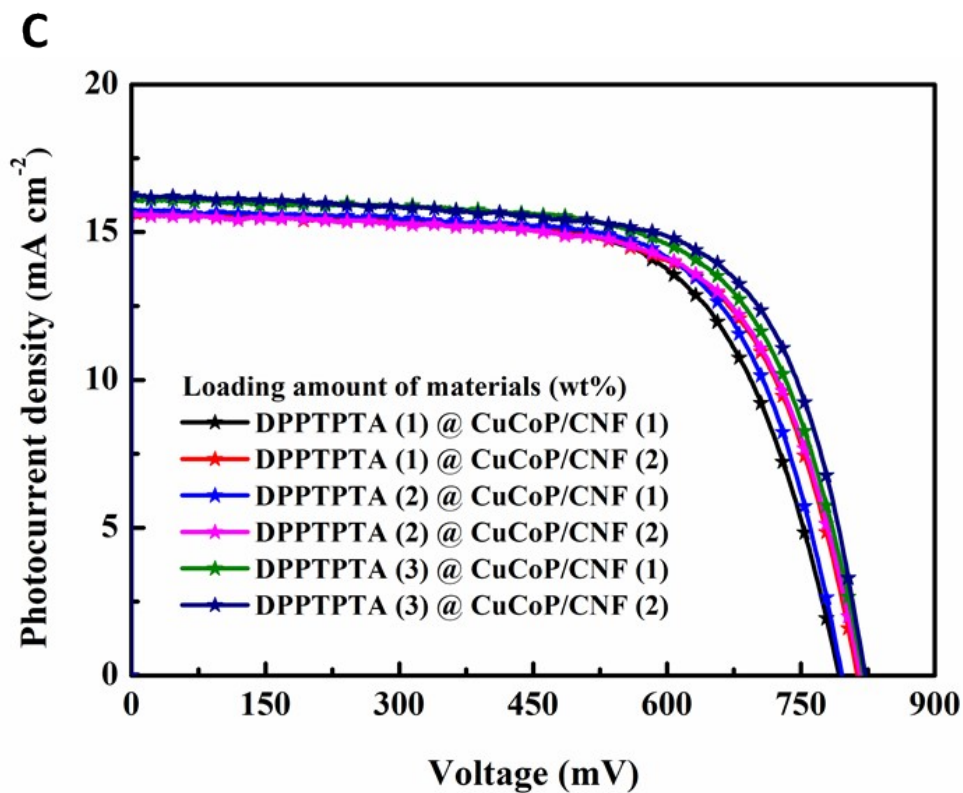
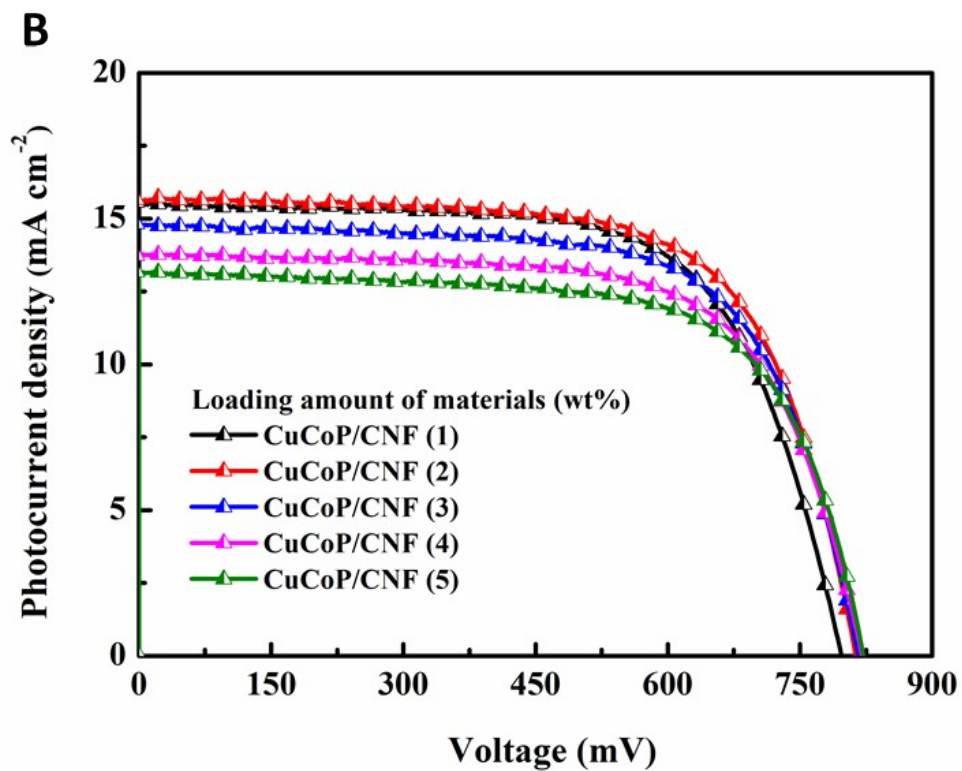


**Fig. S3** Elemental line mapping profile of (A-F) for CuCoP/CNF and (G-O) for DPPTPTA@CuCoP/CNF.



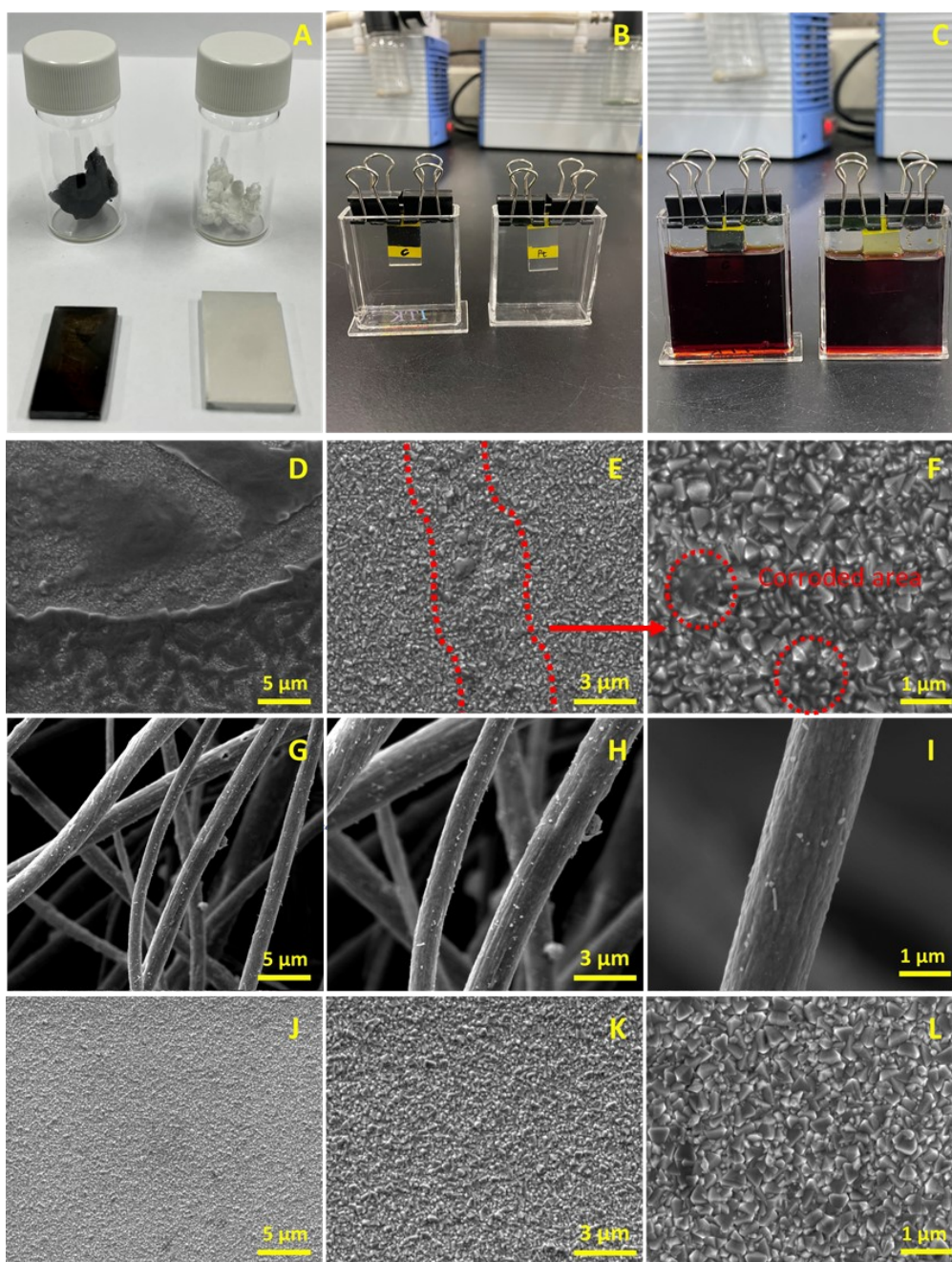
**Fig. S4** Cross-sectional FE-SEM image of DPPTPTA@CuCoP/CNF modified PtCE.





**Fig. S5** The photocurrent density-voltage curves of DSSCs with different loading amounts of (A) bare DPPTPTA, (B) bare CuCoP/CNF, and (C) DPPTPTA@CuCoP/CNF.





**Fig. S6** (A) Visual photograph of white as-spun membrane (before carbonization at 900°C) and bare CuCoP/CNF (black). (B) Visual photograph of the electrode with **DPPTPTA@CuCoP/CNF** modified layer and bare PtCE before soaking in iodide electrolyte for 168 h, and (C) after soaking in iodide electrolyte for 168 h. (D-F) FE-SEM images of bare PtCE after soaking in iodide electrolyte for 168 h. (G-I) FE-SEM images of the electrode with **DPPTPTA@CuCoP/CNF** modified layer after soaking in iodide electrolyte for 168 h. (J-L) FE-SEM images of PtCE after removing the **DPPTPTA@CuCoP/CNF** modified layer after soaking in iodide electrolyte for 168 h.

**Table S1** The photovoltaic performance of DSSCs with DPPTPTA and CuCoP/CNF alone as the modified layers under 1 sun conditions. <sup>a</sup>

Modified layers (wt%)	$\eta$ (%)	$V_{oc}$ (mV)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$
DPPTPTA (1)	8.28 ± 0.03	779 ± 2	15.63 ± 0.02	0.68 ± 0.01
CuCoP/CNF (1)	8.24 ± 0.03	796 ± 1	15.50 ± 0.03	0.67 ± 0.00
DPPTPTA (2)	8.31 ± 0.05	781 ± 1	15.70 ± 0.05	0.68 ± 0.01
CuCoP/CNF (2)	8.59 ± 0.02	813 ± 2	15.61 ± 0.04	0.68 ± 0.00
DPPTPTA (3)	8.53 ± 0.03	793 ± 2	15.86 ± 0.02	0.68 ± 0.02
CuCoP/CNF (3)	8.14 ± 0.02	815 ± 1	14.78 ± 0.02	0.68 ± 0.00
DPPTPTA (4)	8.49 ± 0.02	784 ± 2	16.08 ± 0.06	0.67 ± 0.01
CuCoP/CNF (4)	7.62 ± 0.01	820 ± 2	13.76 ± 0.05	0.68 ± 0.00
DPPTPTA (5)	8.25 ± 0.06	776 ± 1	16.20 ± 0.02	0.66 ± 0.02
CuCoP/CNF (5)	7.47 ± 0.02	827 ± 2	13.20 ± 0.03	0.68 ± 0.00

<sup>a</sup> The standard deviation data for each DSSC are obtained based on three cells.

**Table S2** The photovoltaic performance of DSSCs with DPPTPTA@CuCoP/CNF of different loading amounts as the modified layers under 1 sun conditions. <sup>a</sup>

Modified layers (wt%)	$\eta$ (%)	$V_{oc}$ (mV)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$
DPPTPTA (1) @ CuCoP/CNF (1)	8.26 ± 0.02	791 ± 1	15.66 ± 0.02	0.67 ± 0.01
DPPTPTA (1) @ CuCoP/CNF (2)	8.55 ± 0.02	813 ± 2	15.53 ± 0.05	0.68 ± 0.00
DPPTPTA (2) @ CuCoP/CNF (1)	8.54 ± 0.01	796 ± 2	15.75 ± 0.03	0.68 ± 0.00
DPPTPTA (2) @ CuCoP/CNF (2)	8.58 ± 0.03	815 ± 1	15.58 ± 0.02	0.68 ± 0.01
DPPTPTA (3) @ CuCoP/CNF (1)	8.91 ± 0.04	820 ± 1	16.08 ± 0.04	0.68 ± 0.00
DPPTPTA (3) @ CuCoP/CNF (2)	9.50 ± 0.02	827 ± 2	16.25 ± 0.02	0.71 ± 0.00

<sup>a</sup> The standard deviation data for each DSSC are obtained based on three cells.