Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Self-assembly of Pendant Functional Groups Grafted PEDOT as Paracetamol Detection material †

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Experimental Section

Materials

3-Chloro-1,2-propanediol, 2-methoxythiophene, sodium acetate, potassium thioacetate, potassium acid phthalate, potassium hydroxide, hydrochloric acid and hydrazine hydrate were purchased from Shanghai Chemical Reagents Corporation (Shanghai, China). Toluene, tetrahydrofuran (THF), dichloromethane (DCM) and N,N-dimethylformamide (DMF) were obtained from the same source as described above. Among these chemicals, toluene needed to be further purified, whereas the other analytically pure reagents were used directly. Phosphoric acid buffer solution (PBS) (pH = 7) was obtained by mixing Na_2HPO_4 and NaH_2PO_4 solutions.

Characterization

FTIR spectra of the samples were recorded using an FTIR spectrometer (BRUKER-QEUINOX-55) and KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB 250Xi spectrometer (Al Kα ~ 1486.6 eV). The morphology and microstructure of the samples were investigated by scanning electron microscopy (SEM, SO8010, Japan) and transmission electron microscopy (TEM, JEOL, model 2100). X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 diffractometer with a monochromatic Cu-Kα radiation source (λ = 0.15418 nm), and the scan range (2θ) was 10° to 80°.

Monomer Synthesis (the synthesis route of monomers is shown in fig. S1)

The ^{1}H-NMR data for EDOT is shown in Fig. S2(A)

EDOTCH$_2$Cl: 3,4-dimethoxythiophene (1.64 g, 5.7 mmol), 3-chloro-1,2-propanediol (2.6 g, 12 mmol), toluene (28 mL) and p-toluene sulfonic acid monohydrate (0.16 g, 0.42 mmol) were added sequentially to a two-neck flask. The mixture was stirred at 95°C for 24 h under a nitrogen atmosphere. And, 3-chloro-1,2-propanediol (2.6 g, 12 mmol) was added again to the mixture, and the mixture was refluxed for an additional 3 h at 95°C. After removal of the solvent, a white solid (yield 60%) of chloromethyl-EDOT was obtained by column chromatography (silica gel, volume ratio of hexane/DCM = 4:1).

EDOTCH$_2$NH$_2$: Chloromethyl-EDOT (2 g, 1 mmol) and potassium acid phthalate (3 g, 1.5 mmol) were added to N,N-dimethylformamide (DMF, 100 mL). Then, the mixture was refluxed for 10 h at 80°C, cooled to room temperature and extracted with DCM (30 mL). The organic phase was dried using anhydrous magnesium sulfate, and acid phthalate-CH$_2$EDOT was obtained under reduced pressure. Third, the second product (1.6 g, 5.3 mmol) and hydrazine hydrate (8.5 g, 15.9 mmol) were added to absolute ethyl alcohol (64 mL). Then, the mixture was stirred at 80°C for 5 h, cooled to room temperature and extracted with DCM (30 mL). EDOTCH$_2$NH$_2$ was obtained as a yellow oily liquid (yield 60%) by column chromatography (silica gel, volume ratio of methyl alcohol/DCM = 1/8) (the ^{1}H-NMR data for EDOTCH$_2$NH$_2$ is shown in Fig. S2(B)).

EDOTCH$_2$OH: Chloromethyl-EDOT (1.9 g, 10.0 mmol), CH_3COONa (1.25 g, 15.2 mmol), and dimethyl sulfoxide (DMSO, 30 mL) were added to a 100 mL three-necked flask. The mixture was stirred for 7 h at 120°C, then was poured into water and extracted with DCM. After removing DCM under reduced pressure, a bright yellow oily liquid was obtained and used in the next step. EDOT-MeOAc (1.91 g, 10.02 mmol), 40 mL of KOH solution (1.75 g, 35.0 mmol) was added to in a 30 mL THF solution. This mixture was refluxed for 8 h. Then, 4 mL of HCl was added, this mixture was again refluxed for 7 h. The mixture was further washed, purified and evaporated. EDOTCH$_2$OH was obtained as an ink-green liquid (yield 50%) by column chromatography (silica gel, volume ratio of hexane/acetic ether = 1/1) (the ^{1}H-NMR data for EDOTCH$_2$OH is shown in Fig. S2(C)).

EDOTCH$_2$SH: Chloromethyl-EDOT (1.20 g, 3.1 mmol), thioacetic acid s-potassium salt (1.08 g, 4.7 mmol) and DMSO (6 mL) were added to a 100 mL three-necked flask. The mixture was refluxed for 16 h at 50°C, then it was washed, purified and evaporated, and thioester-EDOT (1.0 g, 2.2 mmol) and sodium methoxide (1.2 M in methanol, 8.0 mL) were added to THF (80 mL). the mixture was stirred at room temperature for 5 h, treated with 5 M HCl, and then extracted with DCM (30 mL). EDOTCH$_2$SH was obtained as a reddish brown liquid (yield 80%) by column chromatography (silica gel, volume ratio of hexane/acetic ether = 1/1) (the ^{1}H-NMR data for EDOTCH$_2$SH is shown in Fig. S2(D)).

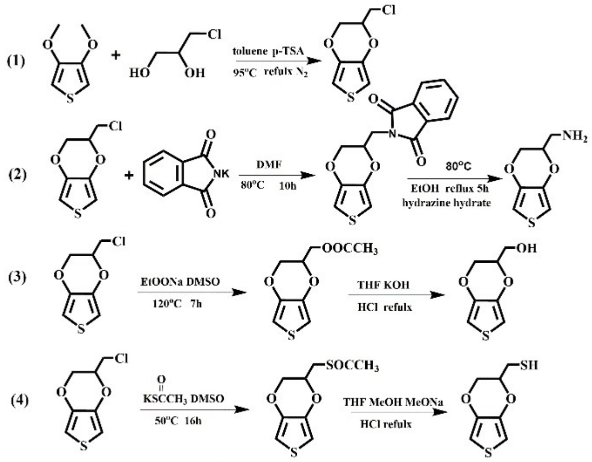

Fig. S1. The synthesis route of monomers

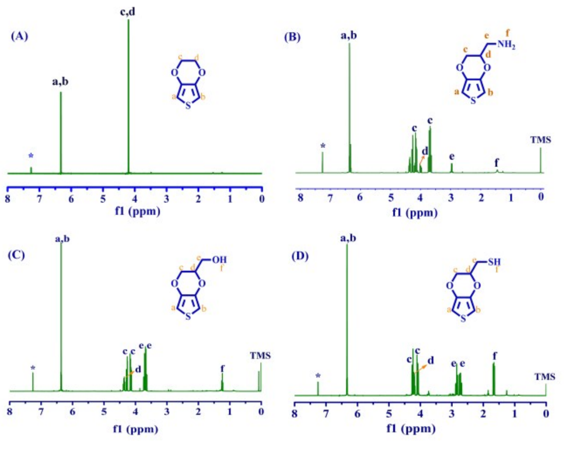

Fig. S2. ^{1}H-NMR of EDOT (A), EDOT CH$_2$NH$_2$ (B) EDOTCH$_2$OH (C) and EDOTCH$_2$SH (D); Starred peak comes from CDCl$_3$

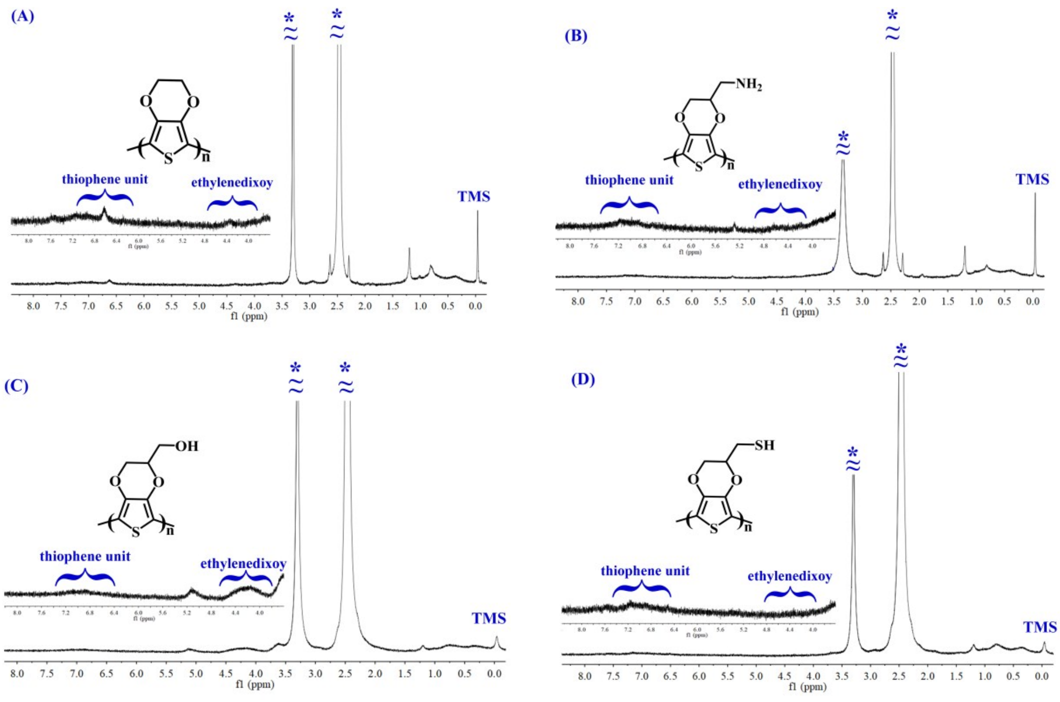

Fig. S3. ^{1}H-NMR spectra of dedope-polymers in DMSO-d6 (treated with 0.2 M $NaBH_4$(aq)); PEDOT (A), PEDOTCH$_2$NH$_2$ (B), EDOTCH$_2$OH (C) and EDOTCH$_2$SH (D); Starred peak comes from H_2O and DMSO-d6

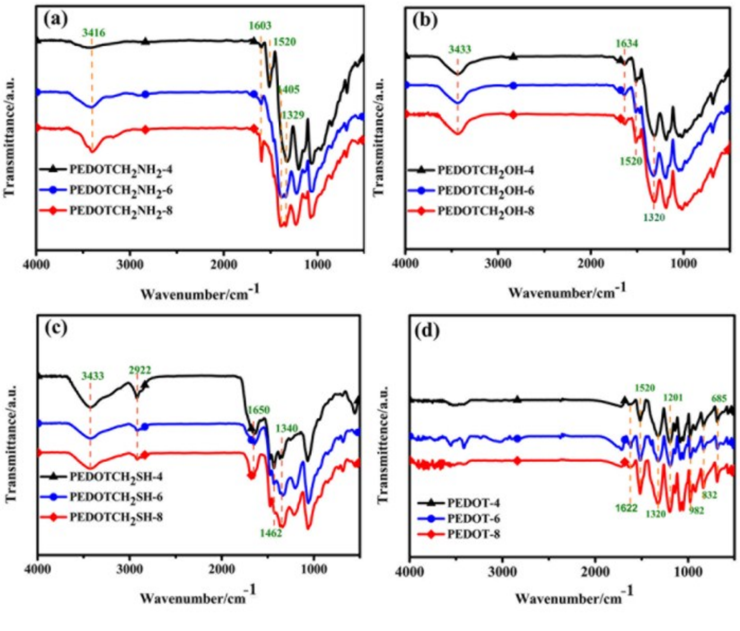

Fig. S4. FT-IR spectra of PEDOTCH$_2$NH$_2$ (a), PEDOTCH$_2$OH (b), PEDOTCH$_2$SH (c) and PEDOT (d); the molar ratios of monomer to $FeCl_3$ are 1:4, 1:6 and 1:8

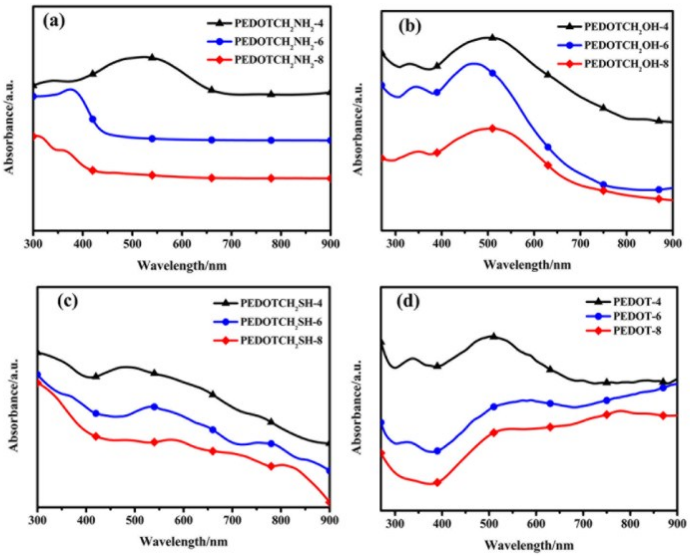

Fig. S5. UV–vis absorption spectra of PEDOTCH$_2$NH$_2$ (a), PEDOTCH$_2$OH (b), PEDOTCH$_2$SH (c) and PEDOT (d); the molar ratios of monomer to FeCl$_3$ are 1:4, 1:6 and 1:8

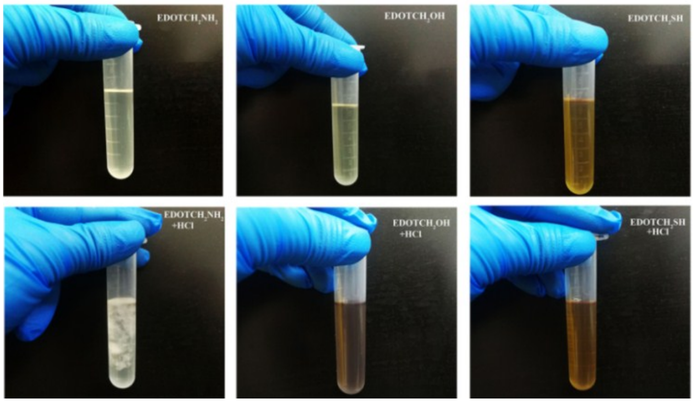

Fig. S6 The salt-formation phenomenon of each monomer in HCl solution

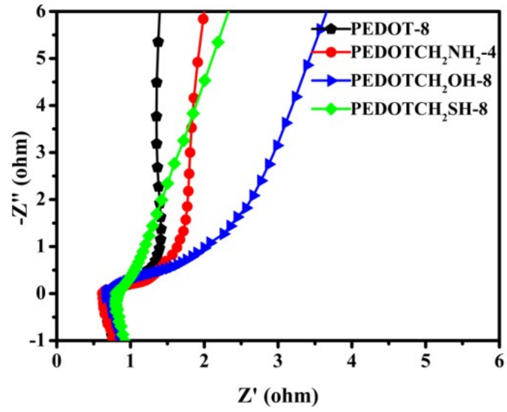

Fig. S7. The Nyquist Plots of PEDOTCH$_2$NH$_2$-4, PEDOTCH$_2$OH-8, PEDOTCH$_2$SH-8 and PEDOT-8: the molar ratios of monomer to FeCl$_3$ are 1:4 and 1:8; the applied potential: 0.61 V, amplitude: 5 mV and frequency range: 0.01-100 KHz.

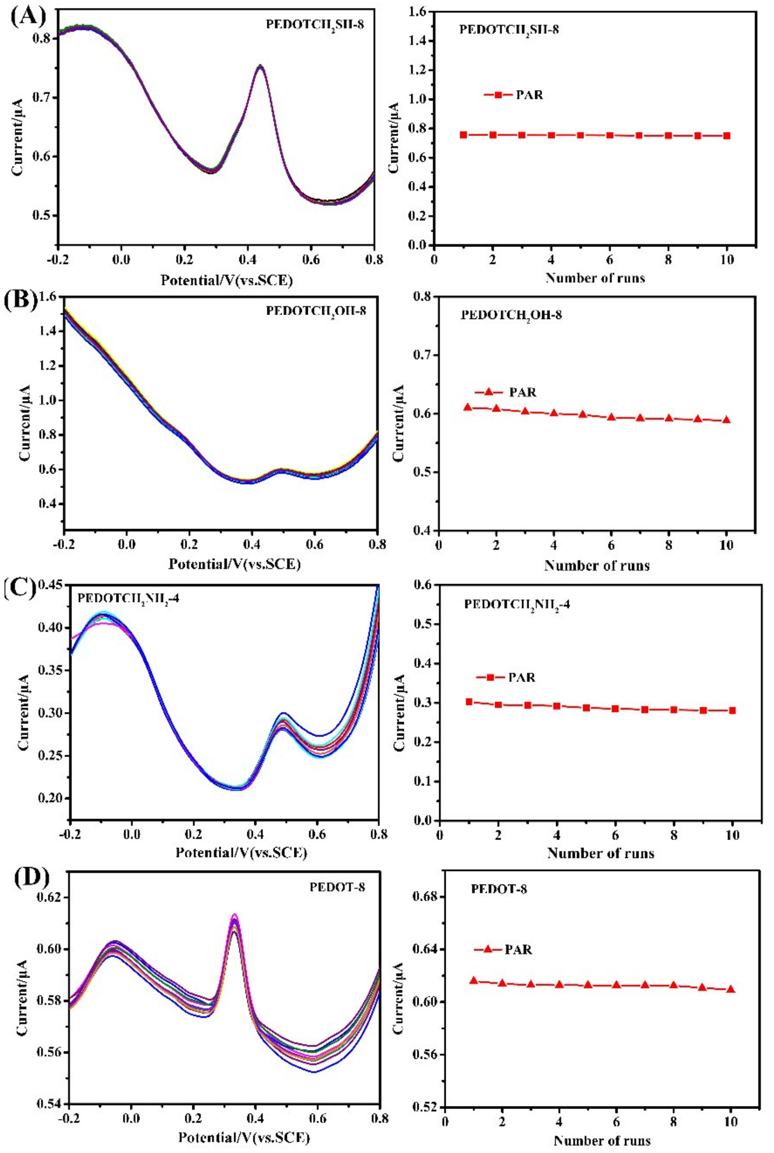

Fig. S8 the reproducibility with PEDOTCH$_2$SH-8(A), PEDOTCH$_2$OH-8(B), PEDOTCH$_2$NH$_2$-4(C) and PEDOT-8-modified GCE(D) in a solution of 0.2 M PBS (PH = 7) containing 4 μM PAR