**Supporting Information** for

# Synthesis of Conducting Polymer Hydrogels with 2D Building Blocks and Its Potential Dependent Gel-Sol Transitions

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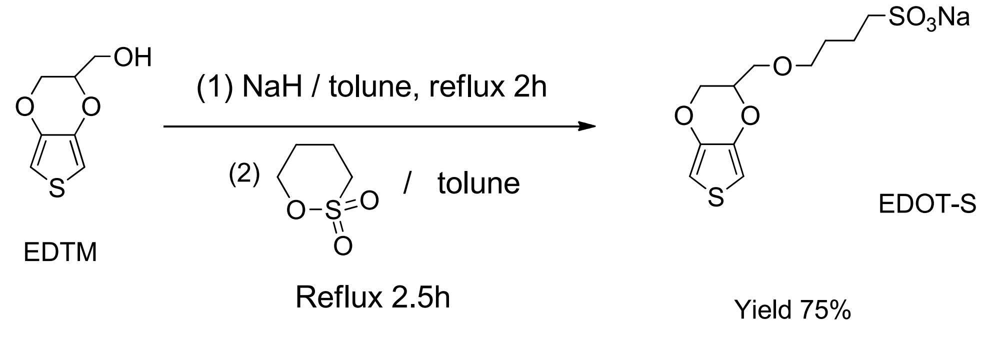
## Experimental

**Materials**: (2,3-dihydrothien [3,4-b][1,4]dioxin-2-yl) methanol (EDTM) and butane sulfone were purchased from Nanjing Clasien Pharmaceutical & Chemical Co., Ltd and Wuhan Fengfan Chemical Co., Ltd., respectively. Other regents were purchased from Beijing Chemical Reagents Company with their purity being of analytical grade and used as received.

**Synthesis**:



Scheme 1: The synthetic route for monomer EDOT-S

**(1) Synthesis of sodium 4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxybutane-1-sulfonate (EDOT-S)**: EDOT-S was synthesized based on the literature reported elsewhere (Stephan, O.; Schottland, P.; Le Gall, P. Y.; Chevrot, C.; Mariet, C.; Carrier, M. *J. Electroanal. Chem.* **1998**, *443*, 217-226; Yamada, M.; Ohnishi, N.; Watanabe M.; Hino Y. *Chem. Commun.* **2009**, 7203-7205). Typically, sodium hydrate (0.5746 g, 16.74 mmol) and (2,3-dihydrothien

[3,4-b][1,4]dioxin-2-yl) methanol (2.5000 g, 14.51 mmol) were mixed in 45 mL toluene under vigorous agitation. After removing oxygen via 20-minutes nitrogen blowing, the resultant ivory emulsion was refluxed for 2h. The butane sulfone (1.976 g, 14.51 mmol) in 14 mL toluene was added after the mixture was cooled to ambient temperature. Then the solution was refluxed for another 2.5h. After cooling again, the acetone (225 mL) was poured into mixture with vigorous stirring. Finally the resulting suspension was filtered, and the off-brown powder (3.602 g, 10.90 mmol) was collected after drying at 100℃ under vacuum, giving a yield of 75.14 % .

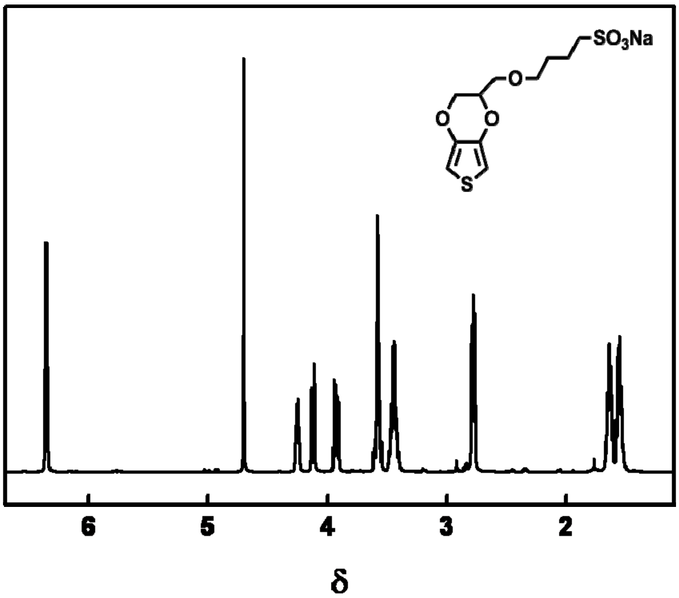


Figure 1: $^1$H-NMR of monomer EDOT-S

The $^1$H-NMR of the monomer in Figure 1 corresponds well with previous reports (Stephan, O.; Schottland, P.; Le Gall, P. Y.; Chevrot, C.; Mariet, C.; Carrier, M. *J. Electroanal. Chem.* **1998**, *443*, 217-226; Yamada, M.; Ohnishi, N.; Watanabe M.; Hino Y. *Chem. Commun.* **2009**, 7203-7205): solvent $D_2O$ (4.70 ppm), 6.36 (2H, s), 4.26 (1H, dd), 4.12 (1H, dd), 3.94 (1H, m), 3.59 (2H, m), 3.44 (2H, m), 2.78 (2H, t), 1.64 (2H, m), 1.55 (2H, m).

**(2) Synthesis of PEDOT-S hydrogels with APS**: in a typical procedure, EDOT-S and 1.2

equiv of APS were mixed in their solid state, and then they were stirred for about 60s after requisite water was added. Finally, the gel was formed after standing for a period of time. The result black gel was washed with a large amount of water for several times to remove low molecular products and other impurities.

**(3) Synthesis of PEDOT-S hydrogels with $FeCl_3$**: in a typical procedure, the prepared EDOT-S monomer (40 mg, 0.12 mmol) dissolved in 0.1mL deionized water, and iron(III) chloride (392.8 mg, 2.42 mmol) in 0.7 mL deionized water were mixed and stirred for ~30s to ensure complete mixing. Subsequently the reaction proceeded without agitation for 24h at room temperature. Then the result black gel was purified by solvent exchange with 0.1 M HCl and water in sequence for several times to remove the excess $FeCl_3$ and other impurities.

**(4) Synthesis of PEDOT-S hydrogels by using the mixture of APS and $FeCl_3$ as an oxidant**: EDOT-S monomer (32.0 mg, 0.097 mmol) was dissolved in 100 μL deionized water. After stirring for a few minutes, a solution of APS (26.5 mg, 0.116 mmol) and $FeCl_3$ (31.43mg, 0.194 mmol) in 0.7 mL deionized water were poured into above solution containing monomers. The mixture was stirred for ~10s before standing. The gel formed within one minute. The resultant hydrogels were washed with water for several times before conducting other experiments or characterizations.

**Instrumentation**: $^1$H-NMR spectra of EDOT-S in $D_2O$ were obtained with an Avance DRX 500 Bruker (500 MHz). SEM images were taken by a Hitachi S-4800 field-emission-gun scanning electron microscope at 5-10 kV. The sample for SEM was prepared by directly putting freezing-dried samples on the conductive tape. AFM (Veeco NanoScope III, Veeco Co., USA) was operated in tapping mode. UV-Vis spectroscopy was performed on UV-6100 double beam spectrophotometer (Shanghai Mapada). X-Ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra spectrometer with a high-performance Al monochromatic source operated at 15 kV. The XPS spectra were taken after all binding energies were referenced to the C 1s neutral carbon peak at 284.8 eV, and the elemental compositions were determined from peak area ratios after correction for the sensitivity factor for each element. Wide angle X-ray powder diffraction patterns of PEDOT-S were measured with a X'Pert Pro MPD (PANalytical, The Netherlands) diffractometer with monochromatic Cu Kα1 radiation ($\lambda$ = 1.5406 Å) at 40 kV and 40 mA. The diffraction patterns were optimized with a step length of 0.01°(2θ ) over an angular range 5-70° (2θ) with a scanning speed of 0.01°/s. Small angle X-ray powder diffraction measurements were conducted with XRD 6000 diffractometer using monochromatic Cu Kα1 radiation ($\lambda$ = 1.5406 Å) at 40 kV and 30 mA. The diffraction patterns were optimized with a step length of 0.01° (2θ) over an angular range 1-10° (2θ) with a scanning speed of 1°/ min. A Keithley 4200 Semiconductor Characterization System was used to measure electrical conductivities (four-probe method) of the samples. Dynamic light scattering measurements were performed with a spectrometer (ALV/DLS/SLS-5022F) using a 22 mW Helium-Neon lasers (632.8 nm wavelength). The scattering angle was 90°, and the intensity autocorrelation functions were analyzed by using the Contin method. Optical images of the samples were observed by the Olympus CX21 optical microscope. Element analysis was conducted on CE440 Elemental Analyzer (Exeter Analytical, Inc, USA). For cryo-TEM experiments, A 5 μL sample was applied to the grid, blotted to a thin film with filter paper, and immediately plunged into liquid ethane (-180 °C) in a Vitrobot cryo-station. Then a cryo-holder (CT 3500) was used to transfer the grid into a FEI Tecnai 20 TEM. The imaging was performed at 200 kV.

## Tables

Table SI1: Standard electrode potentials of different oxidants used in experiments (all the data was estreated from Lange's handbook of chemistry (15th ed.; Dean, J.A.; New York, 1999; pp 8.124-8.139)

| Oxidant | Standard Electrode Potentials / V |
|---|---|
| $(NH_4)_2S_2O_8$ | 1.96 |
| $H_2O_2$ | 1.763 |
| $Ce(SO_4)_2$ | 1.72 |
| $K_2Cr_2O_7$ | 1.36 |
| $HNO_3$ | 0.803 |
| $AgNO_3$ | 0.7991 |
| $FeCl_3$ | 0.771 |
| $Cu(SO_4)_2$ | 0.340 |

Table SI2. Conductivities of the resulting conducting polymer hydrogels in the wet and dry state. The relatively high conductivities of hydrogels in wet state are contributed to both of electronic conductivity and ionic conductivity originated from the electrolyte nature of PEDOT-S, similar to those observed for PEDOT-PSS hydrogel (see References: (1) T.Y. Dai, X.T. Qing, Y. Lu, Y.Y. Xia, Polymer 2009, 50, 5236; (2) L. Chen, B. S. Kim, M. Nishino, J. P. Gong and Y. Osada, Macromolecules 2000, 33, 1232)

| State of samples<br>conductivity S/m<br>Oxidants | Wet hydrogel | Compressed dry pellet |
|---|---|---|
| APS | 154.4 ($\mathbf{C}_{\text{monomer}}$=240 mg/mL) | 90.0 |
| APS + $FeCl_3$ | 25.7 ($\mathbf{C}_{\text{monomer}}$=40 mg/mL) | 1412.2 |
| $FeCl_3$ | 3.0 ($\mathbf{C}_{\text{monomer}}$=40 mg/mL) | 99.1 |

**Figures**

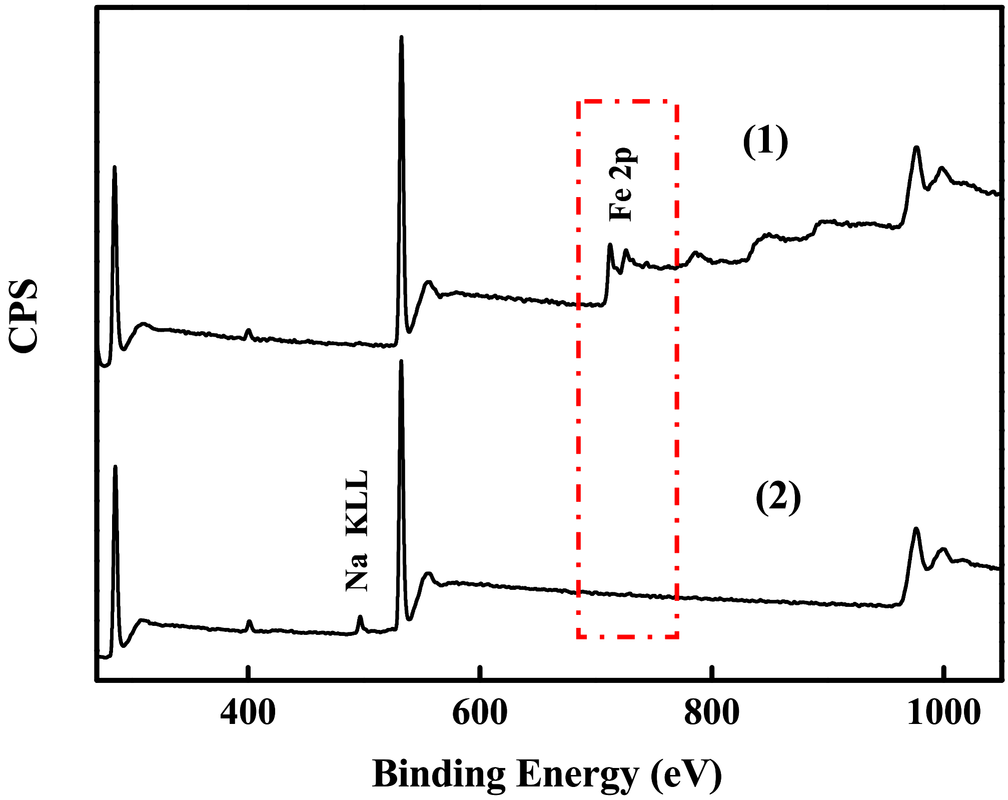


Fig. SI1. XPS spectra of gels synthesized with (1) $FeCl_3$ and (2) APS after freeze-drying, the existence of a small amount of Fe after washing can attribute to the electrostatic interaction between iron cations and negative-charged sulfonic groups.

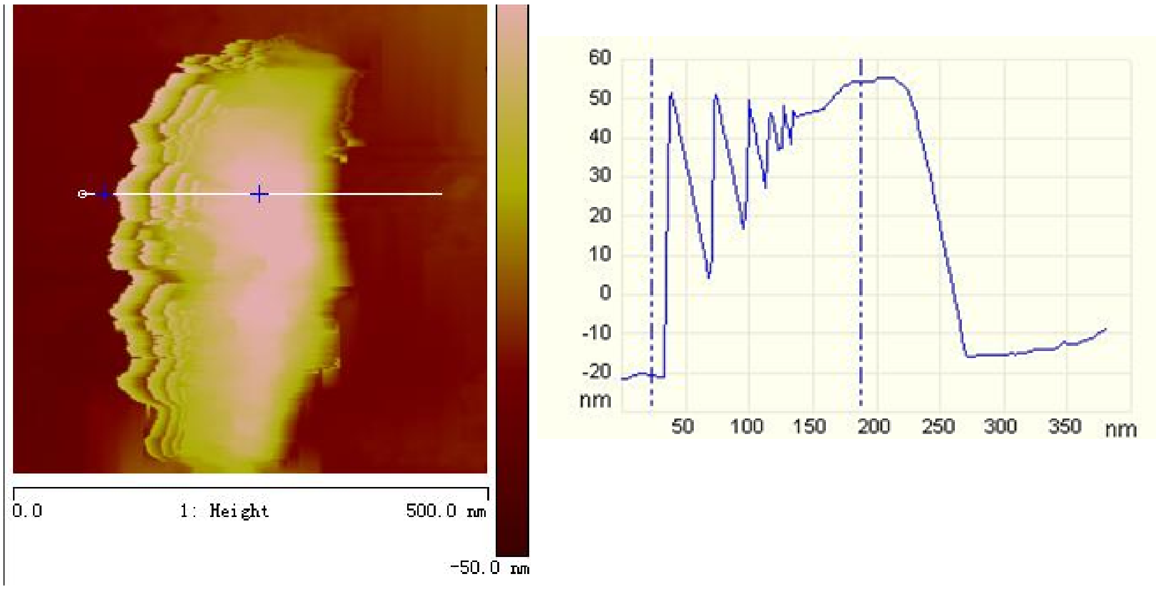


Fig. SI2. AFM image of hydrogels formed by using APS as oxidant when the monomer concentration was 240 mg/mL

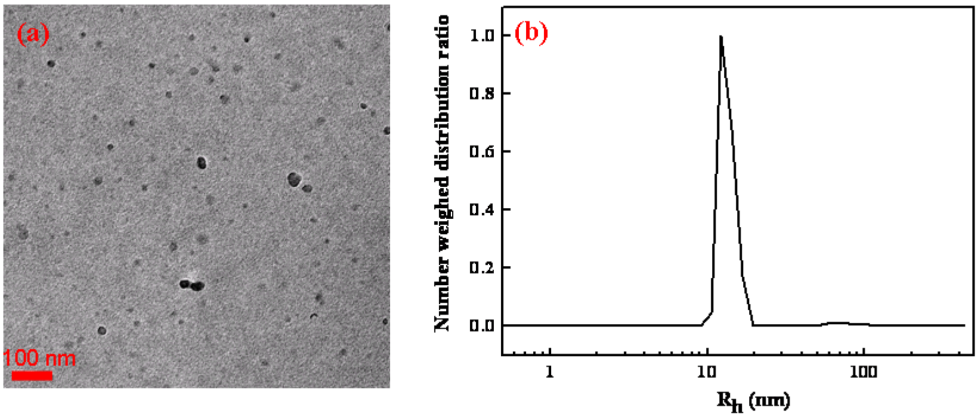


Fig. SI3. The Cryo-TEM image (a), and hydrodynamic radius distribution obtained by dynamic lighting scattering (b) of EDOT-S aqueous solution

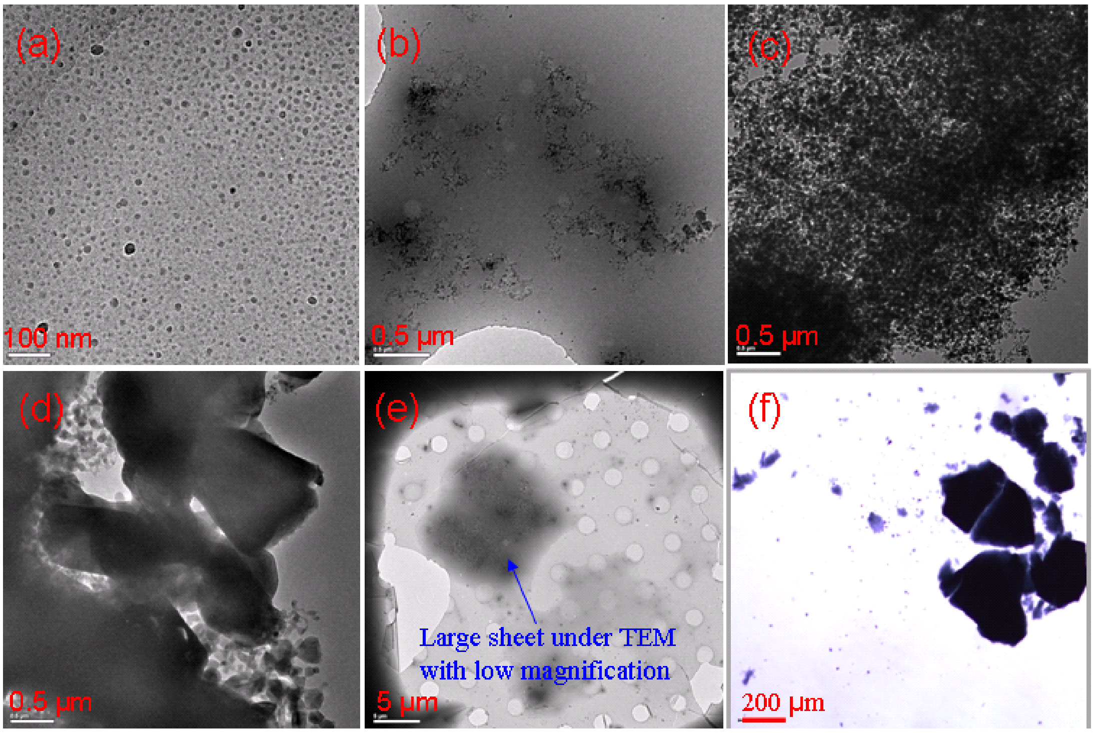


Fig. SI4. Real time observation of EDOT-S solution in the concentration of 240 mg/mL mixed with APS in different stage under cryo-TEM: (a) immediately sampling after mixing, the spherical micelles were clearly recognized; (b) 3 minutes later, the gathering of spherical micelles happened; (c) 9 minutes later, the spherical micelles further aggregated; (d) 19 minutes later, the fuse of the spherical micelles was observed; (e) 29 minute later, the fused micelles evolved into sheet-like square structures with length of ca. 1 μm, and (f) the final product observed under optical microscope

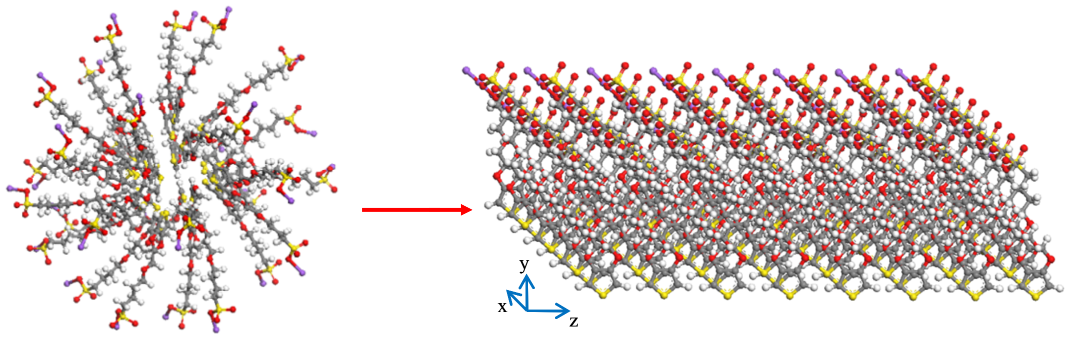
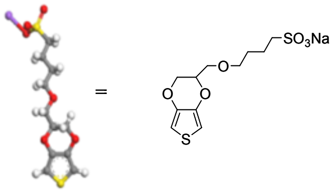


Fig. SI5. Proposed model accounting for sphere-like monomer micelle turned into huge sheet-like structure during polymerization. The sphere-shape micelle was existed in monomer aqueous before reaction. During the process of polymerization, the former micelle collapsed and resultant polymer intends to give a lamellar structure due to strong $\pi$-$\pi$ interaction. We can see that the polymerization proceeded along Z direction, while $\pi$-$\pi$ stacking was along X direction. In figure



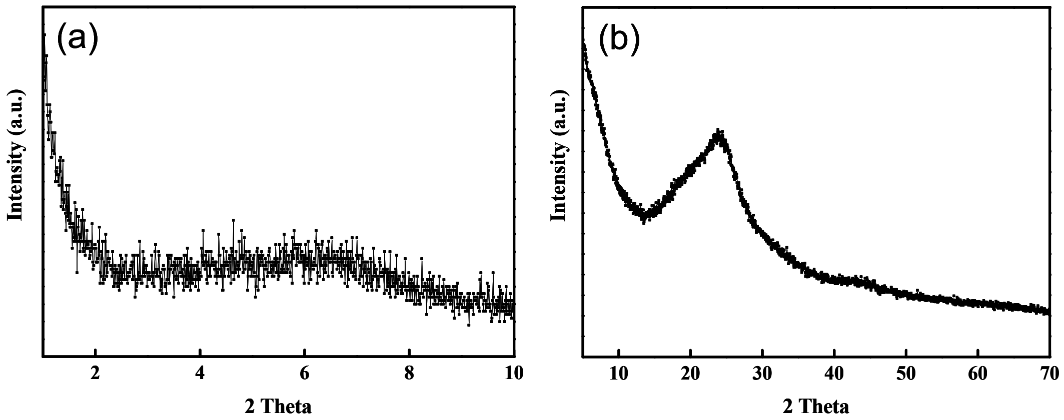


Fig. SI6. The (a) small angle X-ray diffraction (SAXRD) and (b) wide angle X-ray diffraction (WAXRD) patterns of dried hydrogels prepared by using ammonium persulfate as an oxidant. From the XRD patterns, it is clear that the broad peak around 6.5° (13.59 Å) from SAXRD and the peak centered around 24° (3.71 Å) from WAXRD could be attributed to lamellar structure of the hydrogels and interchain π-π stacking of PEDOT-S, respectively (see Reference: Adv. Funct. Mater. 2005, 15, 77). The broad peak in SAXRD may be due to the polydispersity of lamellar distance caused by competitory doping process between sulfonic groups of PEDOT-S itself and anions of used oxidants (chloride ions or sulfate ions) , since the size of dopant ions proved to have some effects on layer distance (see Reference: J. Mater. Chem. 2005, 15, 2077-2088).

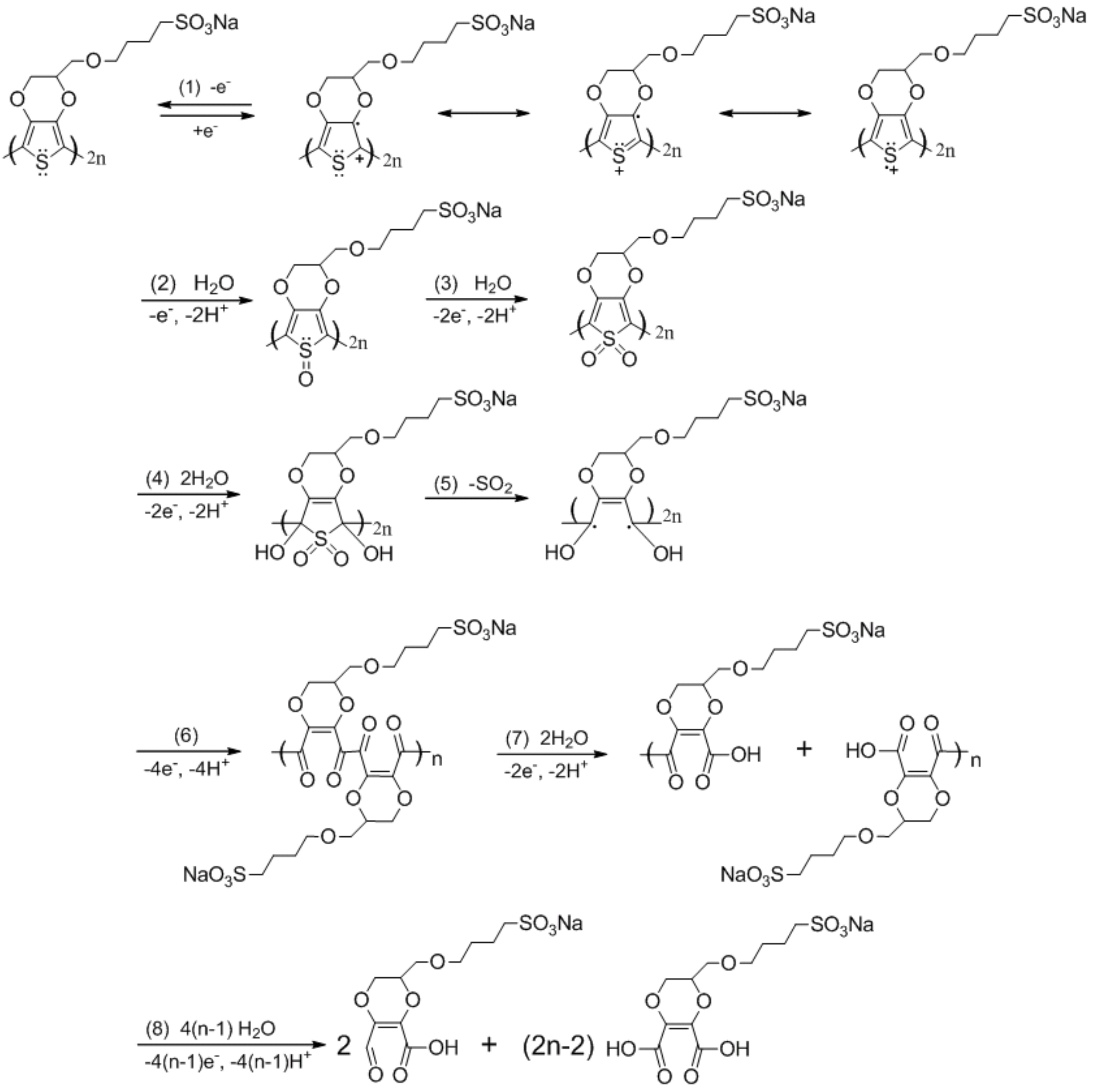


Fig. SI7. Possible overoxidation mechanism of PEDOT-S: The overoxidation process took priority over doped rings of polymer chain. The thiophene ring was opened in the presence of oxidants, and subsequently the conjugated structure was destructed. Finally, polymer chain underwent degradation process and only small molecules were obtained.