Supplementary Information

Kinetic control in the synthesis of highly conductive solution-processable PEDOTs

Ziyi Guo [‡a], Jingming Tang [‡a], Jingyuan Yao [a] and Yuda Li [a*]

[a] Key Laboratory for Green Process of Ministry of Education, Key Laboratory of Novel Biomass-based Environmental and Energy Materials in Petroleum and Chemical Industry, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan, Hubei 430205, China.

[‡] Ziyi Guo and Jingming Tang contributed equal to this work.

*Corresponding authors: E-mail: psydli@wit.edu.cn

1. Experimental Section

1.1 Materials

PSS with M_w of 200 KDa was purchased form Sigma-Aldrich. EDOT monomer was purchased from Sinopharm Chemical. APS, $FeCl_3$, EG, ethanediamine reducing agent and organic solvents including acetone, ethanol were purchased from Sinopharm Chemical and used without further purification.

1.2 Synthesis of LOC PEDOT:PSSs

The LOC PEDOT:PSSs were prepared through the oxidative polymerization of EDOT monomer in an aqueous solution containing PSS.

A typical protocol for the synthesis of LOC1 PEDOT:PSS is as follows: The PSS powder was added to 30 mL of deionized water, followed by the addition of a mixture containing EDOT and EG (1:5) under slow stirring conditions for 60 minutes. The pH was then adjusted to 1. Subsequently, APS was added with high-speed stirring (800 rpm). The feed mass ratio of EDOT to PSS is 1:2, while the mole ratio of APS to EDOT is set at 1.5:1. The above mixture was stirred at room temperature for a duration of 24

h and subsequently subjected to dialysis using a membrane with a molecular weight cutoff of 1000 Da for a period of 5 days. Finally, the PEDOT aqueous dispersion was concentrated to a mass concentration of 1.3% through the process of rotary evaporation. By conducting the oxidative polymerization without the employment of EG, the LOC2 PEDOT:PSS product was obtained. The LOC3, LOC4, and LOC5 PEDOT:PSSs were prepared without the use of EG but instead utilizing $FeCl_3$. $FeCl_3$ was introduced into the reaction system after the addition of APS. The $FeCl_3$ quantities used for the synthesis of LOC3, LOC4, and LOC5 PEDOT:PSSs were 0.1 mol% eq., 1 mol% eq. and 20 mol% eq., respectively ($FeCl_3$:EDOT = 0.001:1, 0.01:1, 0.2:1).

1.3 Preparation of the samples for the UV-vis-NIR studies

The mixture (0.2 mL) at a specific stage of the reaction was initially extracted and transferred into a dialysis bag with a M_w cut-off of 1000 KDa. Then, the extracted mixture underwent dialysis against an abundant supply of distilled water for a duration of three hours, with the water being refreshed every two minutes. As a result, the monomers, oxidizing agents, and salts were effectively eliminated, leading to the acquisition of a purified intermediate suitable for spectral analysis.

1.4 Reducing dedoping procedure

To meet the requirements of M_w analysis, we performed a thorough reducing dedoping treatment on PEDOT intermediates. Specifically, the intermediates (0.3 mL) were initially introduced into 3 mL of a 10 M NaOH solution. Subsequently, 0.3 mL of a strong reducing agent, ethanediamine,[1] was added to the aforementioned solution. Following vigorous stirring at 1000 rpm for a duration of 30 minutes, the thoroughly reduced PEDOT (neutral PEDOT) was successfully obtained.

1.5 H_2SO_4 post-treatment process

The initial step involves spin-coating PEDOT:PSS aqueous dispersions onto glass substrates at 2000 rpm for 60 s. The films were subsequently annealed on a hot plate under ambient atmosphere. Afterwards, the films were immersed in 98% H_2SO_4 and then rinsed with DI water three times. Then, the films were annealed on a hot plate under ambient atmosphere. Next, the films were immersed in 98% H_2SO_4 once again and rinsed with DI water three times. Finally, the films underwent new round of

annealing treatment.

1.6 Measurements and characterizations

UV-vis-NIR absorption spectra were recorded on a UV-3100 UV-VIS spectrophotometer. The HOMO and LUMO energies of thiophene oligomers were computed using Density Functional Theory (DFT) with the B3LYP functional and 6-311G(d,p) basis set as implemented in the Gaussian 09 software package. XPS tests were conducted on a Thermo Scientific ESCALAB 250Xi instrument. Raman spectra were recorded on a DXR Raman Microscope. AFM measurements were performed using Park XE-100 instrumen. TEM measurements were performed on a Tecnai G^2 F30 S-Twin microscope. Electrical conductivities were measured by four-point probe method. Film thicknesses were measured with a Dektak150 step profiler.

2. Supplementary figures and tables
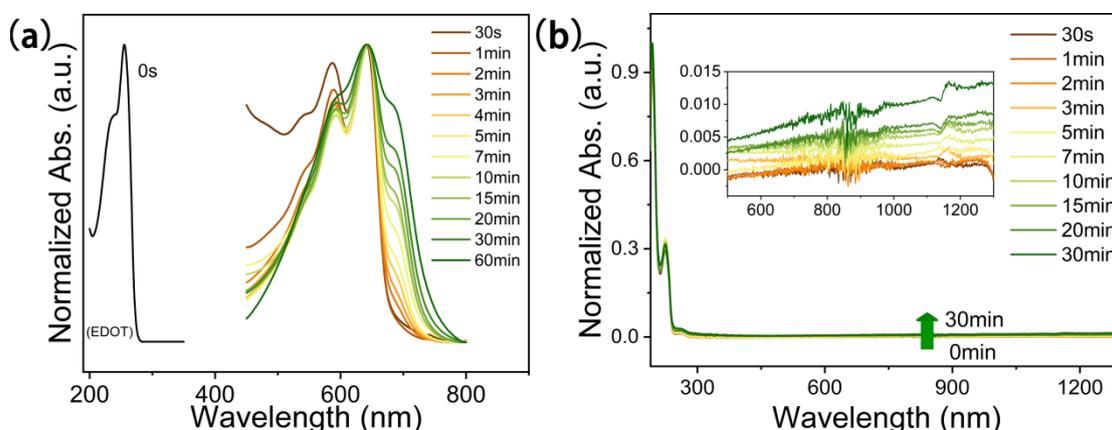
Figure S1 (a) Visible absorption spectra of reaction intermediates during the early stages (0-60 min) after complete dedoping treatments. (b) UV-vis-NIR absorption spectra of the reaction mixtures extracted at early stages (0-60 min). Insert: Enlarged spectra of long-wavelength regions. It should be point out that the initial intermediates used for M_w analysis were not subjected any purification treatments, with the aim of preserving the potential generated oligomers with low M_ws. In contrast, the initial intermediates used for doping degree analysis underwent a rapid dialysis purification process to remove EDOT monomers, oxidizing agents, and salts.

Figure S2 Photographic demonstration of the dissolution cases involving 0.1 g of ammonium persulfate in 10 mL of water (left) and ethylene glycol (right).

Figure S3 Photographic demonstration of the droplets of neat EDOT and EDOT/EG mixture (v/v 1/5) in water.
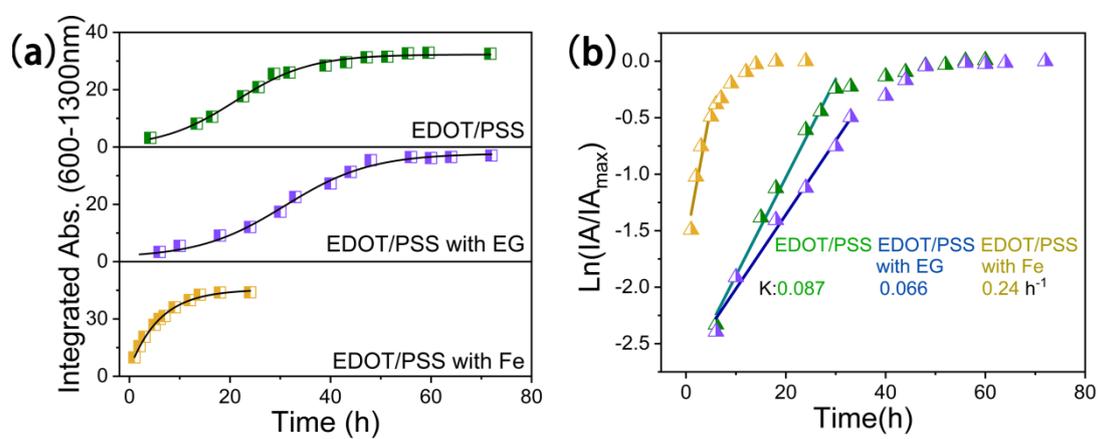
Figure S4 (a) Temporal evolution of the integrated absorbance of polarons in **Fig. 1f, h, j** for various reaction systems. (b) Reaction kinetics for various reaction systems. The IA and IA_{max} are the integrated absorbance of polarons between 700 and 1300 nm depicted **Fig. 1f, h, j** at a specific time and endpoint, respectively.
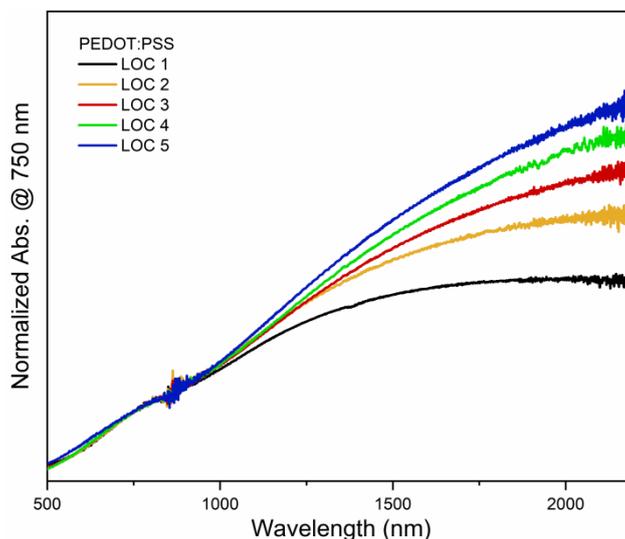
Figure S5 Vis-NIR absorption spectra of various PEDOT:PSS films.
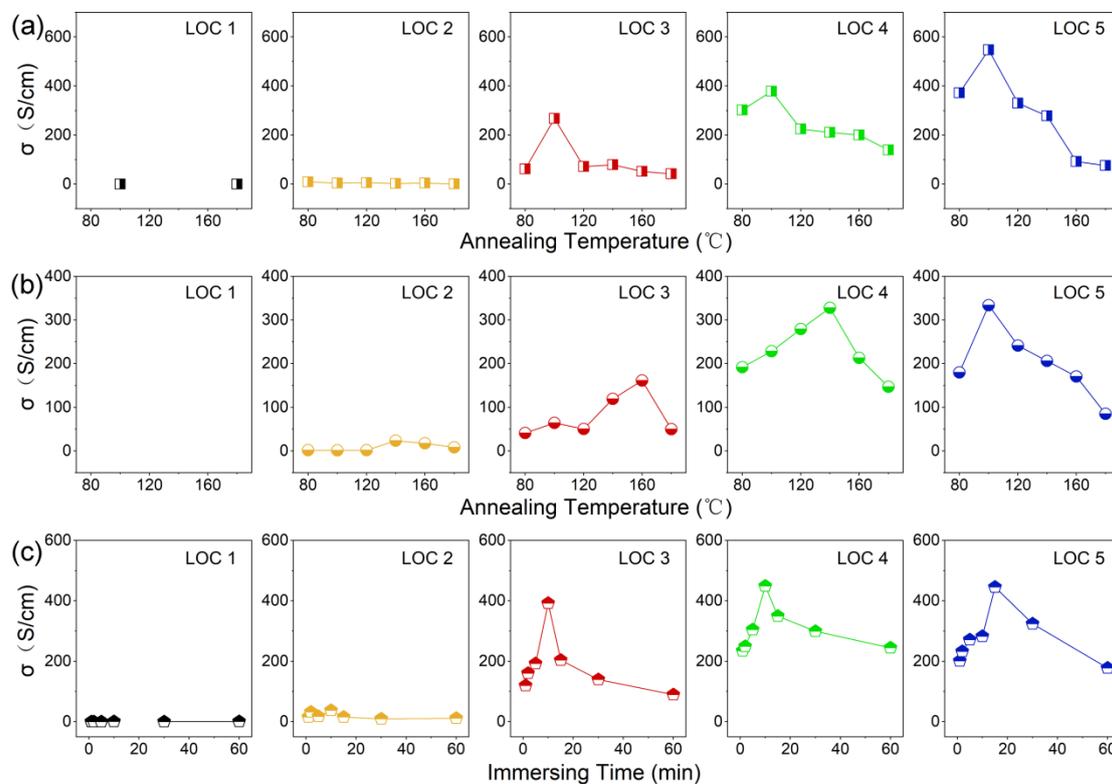
Figure S6 Optimization of the H_2SO_4 post-treatment process. Annealing temperatures

of PEDOT:PSS films prior to (a) and subsequent to (b) H_2SO_4 post-treatment. (c) Immersion time in H_2SO_4.

3. Supplementary References

[1] T. P. A. van der Pol, S. T. Keene, B. W. H. Saes, S. C. J. Meskers, A. Salleo, Y. van de Burgt and R. A. J. Janssen, J. Phys. Chem. C, 2019, 123, 24328–24337.