

Supporting Information

Conducting Redox Polymers with non-Activated Charge Transport Properties

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Experimental Procedures

Electrochemical Quartz Crystal Microbalance (EQCM) studies

EQCM is a useful tool to track the mass of conducting polymers with different doping levels.

The mass of the PDeTeT film during electrochemical redox conversion was recorded by EQCM measurements, using a VersaSTAT3 potentiostat (Princeton Applied Research, AMETEK, Inc. United States) equipped with a QCM module (QCM922A). Cyclic voltammetry was used to prepare the polymer film on a QCM922 crystal and the resulting film was examined in a monomer free MeCN solution containing 0.1 mol L⁻¹ TEAPF₆ by cyclic voltammetry at 0.05 V s⁻¹. The mass changes during electrochemical redox conversion of the polymers were calculated using the Sauerbrey equation:

$$\Delta mass = \frac{-\Delta freq \times A \times \sqrt{\mu q \times \rho q}}{2(Fq)^2}$$

where $\Delta freq$ is the resonant frequency change, A is the area of active surface (0.198 cm²), μq is the AT-cut quartz constant (2.947 × 10¹¹ g cm⁻¹ s⁻²), ρq is the quartz crystal density (2.65 g cm⁻²) and Fq is the reference frequency for the crystal (8.95 MHz).

Results and Discussion

EQCM

PDeTeT was cycled in different doping potential regions as shown in Figure S1. The polymer was firstly cycled in p-doping region only. Reproducible mass and current is obtained for the polymer film in this potential region. During these p-doping/dedoping processes, a large number of counterions (PF_6^- with a molar mass of $144.96 \text{ g mol}^{-1}$) and solvent (MeCN with a molar mass of 41.05 g mol^{-1}) is taken up/removed by the polymer matrix to compensate for the oxidized/neutralized thiophene units (the involved number of ions and solvent is shown in Table S1), resulting in the increase/decrease of polymer mass. When the polymer was cycled to the n-doping region (Figure S1b), polymer mass also increases in the beginning of doping. These processes correspond to the up-take of cations (TEA^+ with a molar mass of $130.25 \text{ g mol}^{-1}$) and solvent to charge compensate for the reduction of PDeTeT. However, when the polymer is further reduced the mass of the material drops almost to zero and is only partially regained in the backward scan. In subsequent scans the mass decreases further and the mass curves are distorted. In clear contrast to the mass response the CVs of PDeTeT do not show any dramatic decay or distortions during electrochemical cycling.

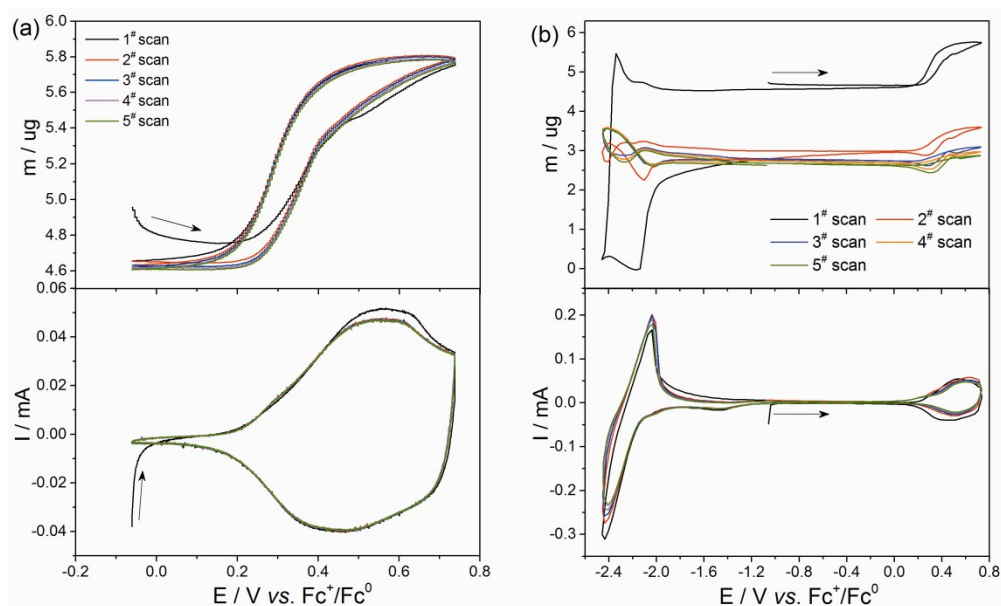


Figure S1. EQCM studies of PDeTeT in different potential regions: (a) in p-doping region of the backbone and (b) in the potential region covering p-doping and subsequent n-doping of the backbone/redox active region of the pendant. Arrows indicate the initial scan direction. Upper figures show the mass of the polymer changes with potential during electrochemical cycling while the lower figures show the corresponding CVs of the material during these measurements.

Table S1. The change of charge number (Δn), mass (Δm) and molar mass (ΔM) of the species involved in the oxidation and reduction of PDeTeT in different potential regions. Scan no. 1-5 show the numbers of each item for different cycles in the p-doping region as shown in Figure S1a. Scan no. 1[#] shows the numbers of each item of the species associated with the first cycle in the n-doping region as shown in Figure S1b (the increase part).

Scan no.	Δn_{ox} (nmol)	Δm_{ox} (μg)	ΔM_{ox} (g mol^{-1})	Δn_{re} (nmol)	Δm_{re} (μg)	ΔM_{re} (g mol^{-1})
1	2.81	0.73	259.8	-7.16	-1.07	149.4
2	1.95	0.72	369.2	-3.53	-1.16	328.6
3	1.89	0.71	375.7	-3.53	-1.17	331.4
4	1.68	0.68	404.8	-3.52	-1.18	335.2
5	1.55	0.65	419.4	-3.54	-1.17	330.5
1 [#]				-15.55	-4.31	277.2

Polymerization on an IDA electrode

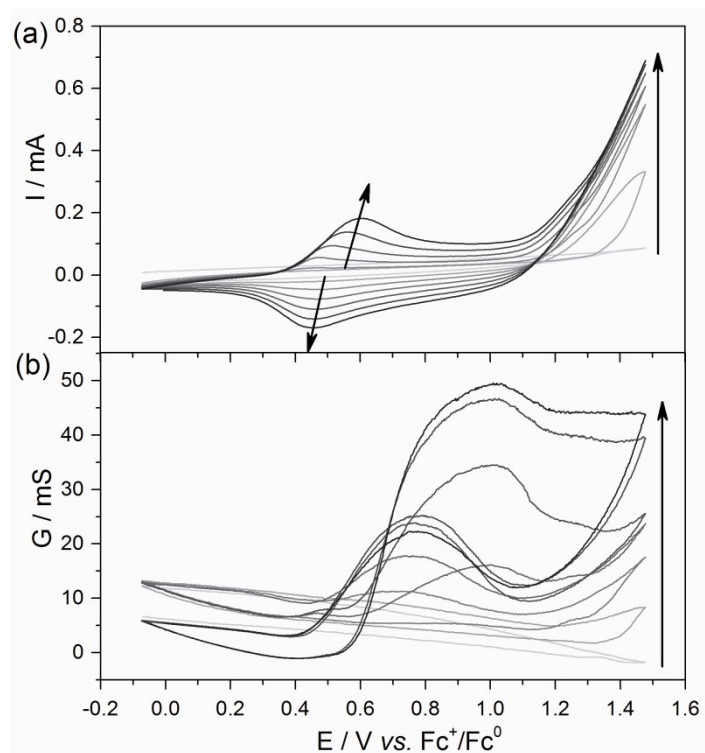


Figure S2. (a) CVs of the electrochemical polymerization of PDeTeT on an IDA working electrode and (b) the corresponding conductance (G) of the material during the polymerization cycling. Arrows indicate the direction of the current/conductance increase during polymerization processes.

Temperature dependent conductance measurements of PT

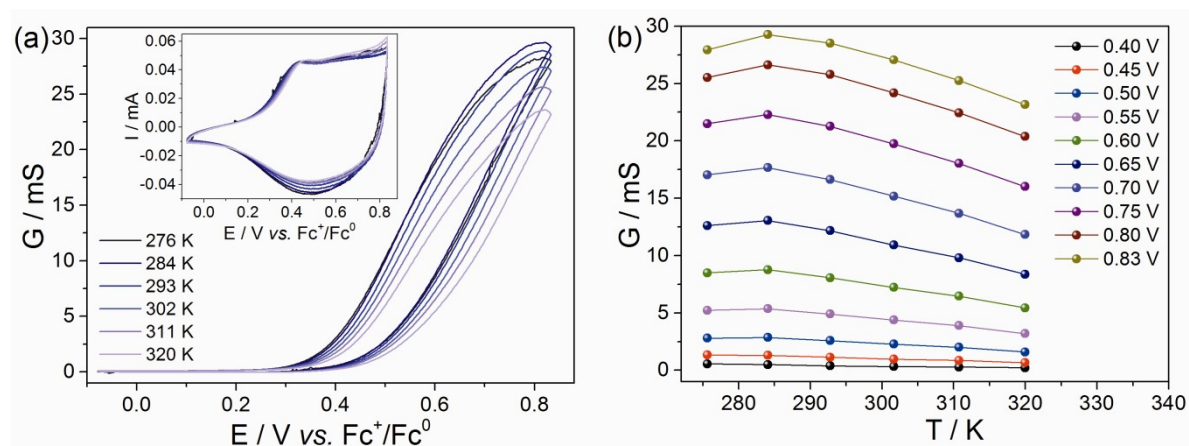


Figure S3. The potential dependence of G of PT in the temperature interval between 276 and 320 K shows a monotonous increase coinciding with the polymer doping onset potential (a). The corresponding CVs of PT are largely unaffected by temperature (inset, panel a). The conductance of polythiophene slightly increases at lower temperatures and then decreases at higher temperatures under study, giving a weak conductance maxima centered at 285 K (b).

EPR

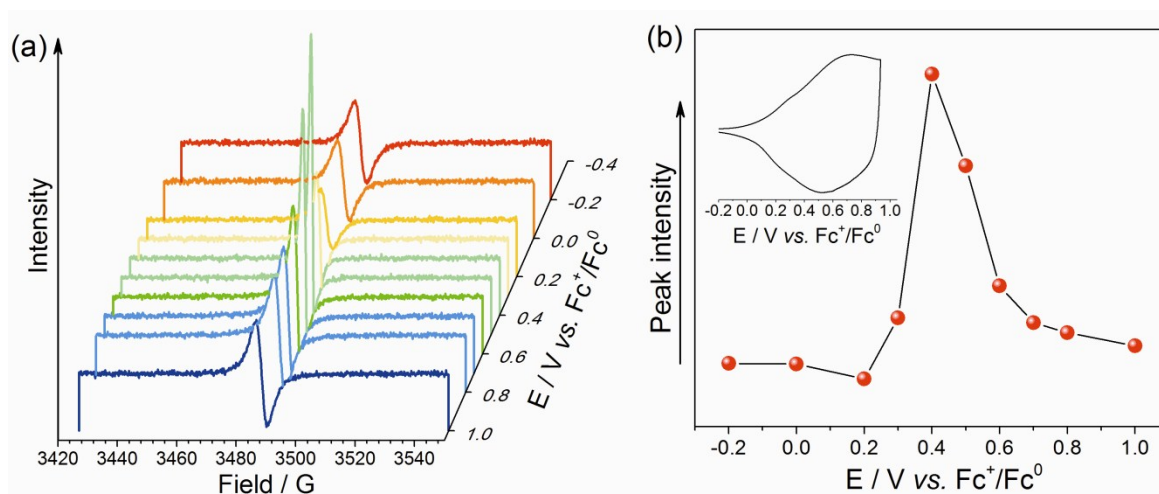


Figure S4. EPR spectra of PT at various doping potentials (a). The spin intensity of free radicals increases in the beginning of doping and then decreases with doping potential, giving a maximum spin intensity of polarons in doped polymer (b). Inset shows the CV of the material on the EPR working electrode.

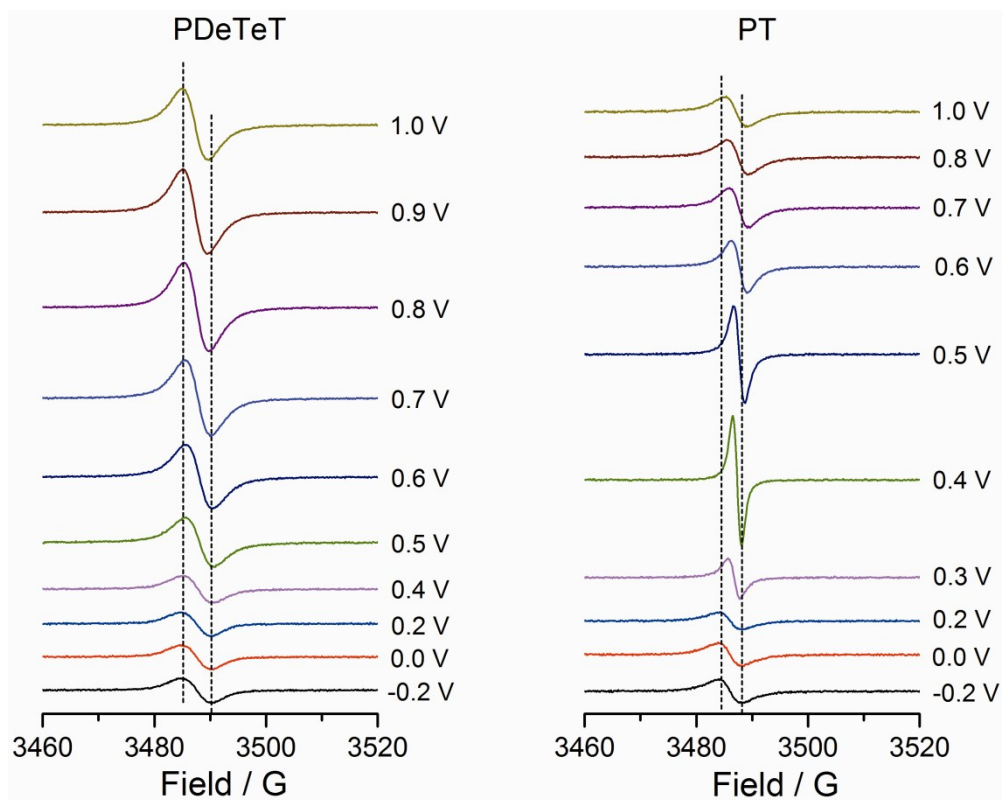


Figure S5. EPR spectra of PDeTeT and PT at various doping potentials. The same y axis interval is used for all curves. The dashed lines show the peak-to-peak linewidth for the radicals at neutral states (i.e. -0.2 V vs Fc⁺/Fc⁰). EPR single can be observed for neutral PDeTeT and PT. This finding suggests that undoped polymers also intrinsically contain radicals in their structure. These radical defects could be formed during polymerization of the material.^[1]

Table S2. The peak-to-peak linewidth of the free radicals formed in PDeTeT and PT at different doping potentials.

Potential / vs Fc ⁺ /Fc ⁰	Peak-to-peak Linewidth / G of PDeTeT	Peak-to-peak Linewidth / G of PT
-0.2	5.6	4.2
0.0	5.6	4.2
0.2	5.5	4.1
0.3	/	2.1
0.4	5.3	1.6
0.5	5.0	2.1
0.6	4.9	2.9
0.7	4.7	3.4
0.8	4.4	3.6
0.9	4.4	/
1.0	4.6	3.9

Set-up of *in situ* ATR-FTIR measurements

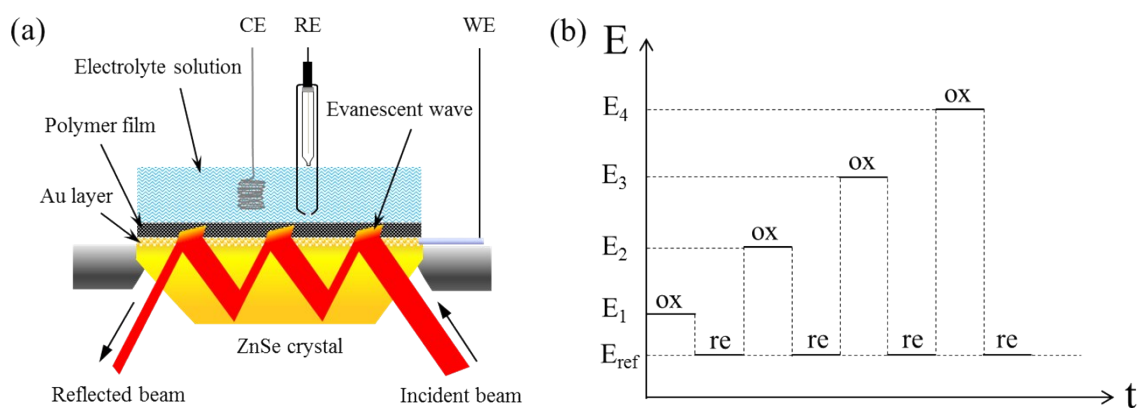


Figure S6. Setup of the ATR-FTIR measurements of PDeTeT in a three-electrode system, CE, counter electrode; RE, reference electrode; WE, working electrode (a).^[2] The profile of potential steps applied during the ATR-FTIR measurements (b).

References

- [1] (a) W.-T. Chen, G. A. Bowmaker, R. P. Cooney, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4218; (b) S. Hyashi, K. Kaneto, K. Yoshino, R. Matsushita, T. Matsuyama, *J. Phys. Soc. Jpn.*, 1986, **55**, 1971.
- [2] C. Kvarnström, H. Neygebauer, A. Ivaska, N. S. Sariciftci, *Journal of Molecular Structure*, 2000, **521**, 271.