Int. J. Electrochem. Sci., 15 **(2020)** 1044 – 1057, doi: 10.20964/2020.02.30

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

A Multi-color Electrochromic Material based on Organic Polymer

Hui Zhang[1], *Shouli Ming*[2], *Yuzhang Liang*[1], *Lei Feng*[1], *Ting Xu*[1,*]

[1] College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China
[2] State Key Laboratory Base of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China
*E-mail: xuting@nju.edu.cn

Received: 8 September 2019 / *Accepted:* 18 November 2019 / *Published:* 31 December 2019

With low-cost and simple processing, organic electrochromic polymers have attracted considerable attention as a promising material platform for flexible and low-energy-consuming optoelectronic devices. However, typical electrochromic polymers can only be switched from natural-colored to oxidized-transparent states. As a result, the complexity of combining several distinct polymers to achieve a multi-color gamut has significantly limited the niche applications of electrochromic polymers. Here we report an electrochromic polymer based on 5,7-bis(3,3-dimethyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (PEP), which exhibits multi-color reversible tuning capability. This organic electrochromic material offers an effective approach to dynamic manipulate color and enables a variety of optoelectronic applications.

Keywords: multi-color; color tuning; single molecular template; conjugated polymer; electrochromic material

1. INTRODUCTION

Electrochromic materials, which show a reversible color change when reduced or oxidized electrochemically by application of a small voltage, have been gaining great interest in academia and industry because of their fascinating spectro-electrochemical properties and practical applications [1-4]. In contrast to the complexity and high-cost of thin film vacuum deposition typically required in the fabrication of inorganic electrochromic devices, such as these with tungsten trioxide, the solution-process technology enables synthesizing conjugated polymers for the mass production of flexible and cost-effective electrochromic materials [5-10]. Therefore, polymer electrochromic devices are particularly attractive for retrofitting onto existing windows for energy savings, as well as for a variety of wearable medical and fashion related applications [11-13]. Unfortunately, most of the typical conjugated polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,4-propyylenedioxythiophene) (PProDOT), can only be switched from natural-colored to oxidized-transparent states [7,14,15]. The monotony of generated colors significantly limits their extended colorful electrochromic applications in the visible spectrum [16,17].

As an important factor evaluating the performance of electrochromic materials, color gamut directly links to the human visual perception and determines electrochromic materials' application scenarios [18,19]. To achieve the electrochromic devices displaying several different colors, most researchers assemble two (or more) kinds of electrochromic materials together to increase the color gamut according to color-mixing theory principles [20-28]. However, the complicated process and the chemical compatibility between different electrochromic materials restrict their practical applications. Compared to processing techniques based on color-mixing theory, different colors of designed polymers have been achieved through incorporation of donor-acceptor systems, modification of steric effects, introduction of heteroatoms, etc. [18, 29-30]. As an alternative method, a single polymer-based full-color electrochromic device has been achieved by employing plasmonic nanostructured electrodes [31]. The working principle of this approach is to use surface plasmon polaritons of nanostructured electrode to filter the spectrum of white light and generate individual colors. Nevertheless, the high-cost associated with fabrication of large-scale nanostructured electrodes represents a significant challenge for mass production.

Our previous work demonstrated that conjugated polymers with planar skeleton exhibit excellent electrochromic performance [30]. It is noteworthy that planar conjugated system can be maintained through intramolecular noncovalent interactions, such as O···S. Considering the O···S interaction between the adjacent EDOT and ProDOT. We designed and synthesized the conjugated polymer poly(5,7-bis(3,3-dimethyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine) (poly(PEP)) with multi-color tunability. To our knowledge, this is the first report on the single polymeric template-based multi-color organic electrochromic material. This single polymeric template-based electrochromic material offers an effective way to dynamically manipulate the color spectrum in the visible range and potentially enable a myriad of optoelectronic applications.

2. EXPERIMENTAL

2.1 Material and Instruments

3,4-dimethoxythiophesssne (98%), 2,2-dimethyl-1,3-propanediol (98%), *p*-toluenesulfonic acid monohydrate (*p*TSA, 99%), 3,4-ethylenedioxythiophene (EDOT, 98%), N-bromosuccinimide (NBS, 99%,), *n*-butyllithium (*n*-BuLi, 2.5 mol L^{-1} in hexanes), tributylstannyl chloride ($SnBu_3Cl$, 98%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), dichloromethane (CH_2Cl_2, 99.8%), chloroform ($CHCl_3$, >99%), toluene (anhydrous, 99.8%), tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$, 99%), tetrahydrofuran (THF, 99.5%), and acetonitrile (ACN, >99%) are purchased commercially from J&K Scientific Ltd. THF and ACN are distilled under nitrogen atmosphere before use. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, for electrochemical analysis, ≥99.0%, Sigma-Aldrich) is dried under vacuum at 80 °C for 24 h before use. Unless otherwise noted, all chemicals are commercially available and used without further purification.

Nuclear magnetic resonance (NMR) spectra are recorded on a Bruker AV 400. High Resolution Mass Spectra (HRMS) is performed using Bruker. Electrochemical experiments are performed on Gamry REF3000-31122 (Gamry Instruments, USA) electrochemical workstation. Absorption spectra are carried out on an Ocean View USB 2000+ H15520 UV-vis-NIR spectrophotometer (Ocean Optics Inc.).

2.2 Electrochemical Experiments

For electrochemical tests, the working electrode is ITO coated glass (9.0 mm × 50.0 mm × 1.1 mm, <10.0 ohm/sq), the counter electrode is platinum wire (1.0 mm), an Ag/AgCl electrode is used as the reference electrode, revealing sufficient stability during the experiments. ACN contains 0.1 mol L^{-1} Bu_4NPF_6 is used as an electrolyte solution. The electrochemical behavior and spectra of the polymer are measured in monomer-free ACN-Bu_4NPF_6 solution.

2.3 Monomer Synthesis

Synthesis of compound 4: A solution of compound 3 (4.0 g, 21.7 mmol) in 100 mL dry THF, cooled to -78°C and blanketed the air in the three-necked bottle by argon atmosphere. Then, 12.8 mL (16.0 mmol) of *n*-BuLi (2.5 M in hexane) slowly added dropwise to the solution within 30 min under argon. The mixture stirred for 1.5 h under -78°C, and then warmed to -40°C. Added tributyltin chloride (11.7 g, 18.0 mmol) slowly to the solution, stirred and then natural warming to room temperature. The mixture is stirred at room temperature and continue to react for 12 h under an argon atmosphere. Next, the mixture is extracted and concentrated under vacuum. The resulting product (9.92 g, yield: 89%) is used directly for the Stille coupling reaction without further purification; ^1H NMR (400 MHz, $CDCl_3$, ppm, Figure S1): δ 6.72 (s, 1H), 3.70 (s, 2H), 3.63 (s, 2H), 1.01 (s, 6H), 1.56 (t, 6H), 1.32 (t, 6H), 1.08 (t, 6H), 0.89 (t, 9H).

Synthesis of PEP: Under a nitrogen atmosphere, to a solution of Compound 6 (1.8 g, 6.0 mmol) and Compound 4 (6.1 g, 13.0 mmol) in dry THF is added $Pd(PPh_3)_4$. The mixture is heated under reflux for another 24 h with vigorous stirring, then, concentrated under vacuum. The compound is separated by silica column chromatography ($CHCl_3$ as the eluent), then obtained the desired yellow green solid PEP (0.62 g, yield: 20%); ^1H NMR (400 MHz, $CDCl_3$, ppm, Figure S2): δ 6.43 (s, 2H), 4.35 (s, 4H), 3.84 (s, 4H), 3.73 (s, 4H), 1.08 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$, ppm, Figure S3): δ 149.97, 144.93, 137.08, 115.76, 108.87, 103.46, 80.61, 80.24, 65.02, 39.12, 21.71. HRMS (MALDI-TOF): m/z Calcd for $[C_{24}H_{27}O_6S_3]^+$ $[M+H]^+$ 507.097; Found 507.009, as shown in Figure S4.

3. RESULTS AND DISCUSSION

Figure 1 shows the synthetic route and electropolymerization of 5,7-bis(3,3-dimethyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (PEP). The removal of one α-proton from compound 3 with *n*-BuLi afforded the anion intermediate, which is quenched by Bu_3SnCl to obtain the compound 4, which is used for the next step without further purification.

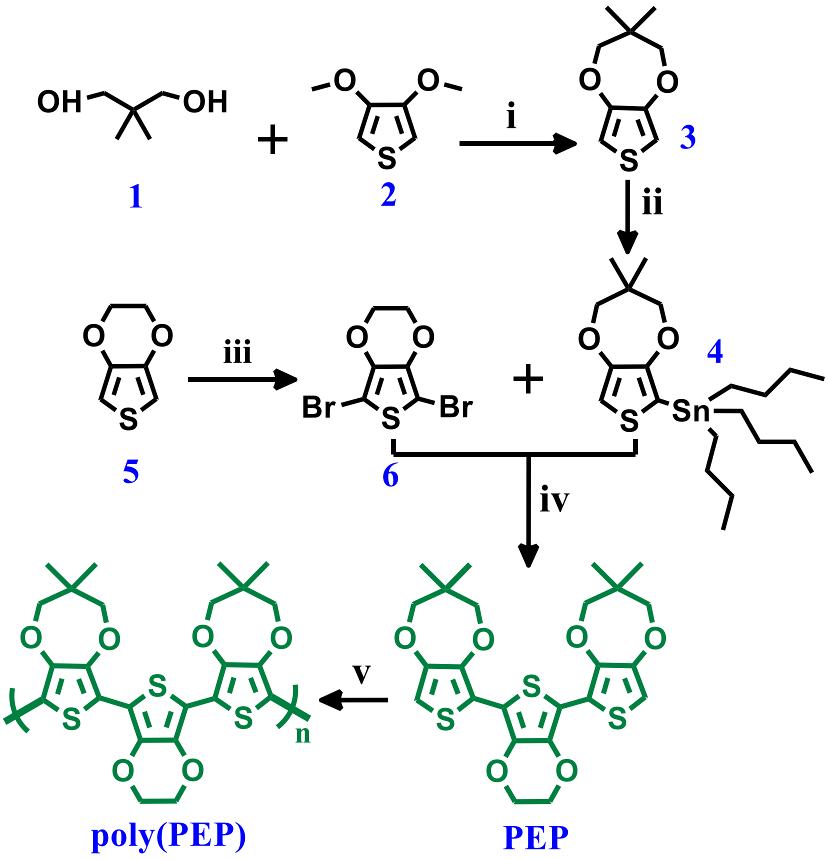


Figure 1. Synthetic route of poly(PEP). (i) *p*-TSA, toluene, 80°C, 56%. (ii) *n*-BuLi, THF, -78°C; Bu_3SnCl, -40°C. (iii) NBS, $CH_3COOH/CHCl_3$, 85%. (iv) $Pd(PPh_3)_4$, THF, refluxing, 20%. (v) ACN-Bu_4NPF_6, electrochemical polymerization.

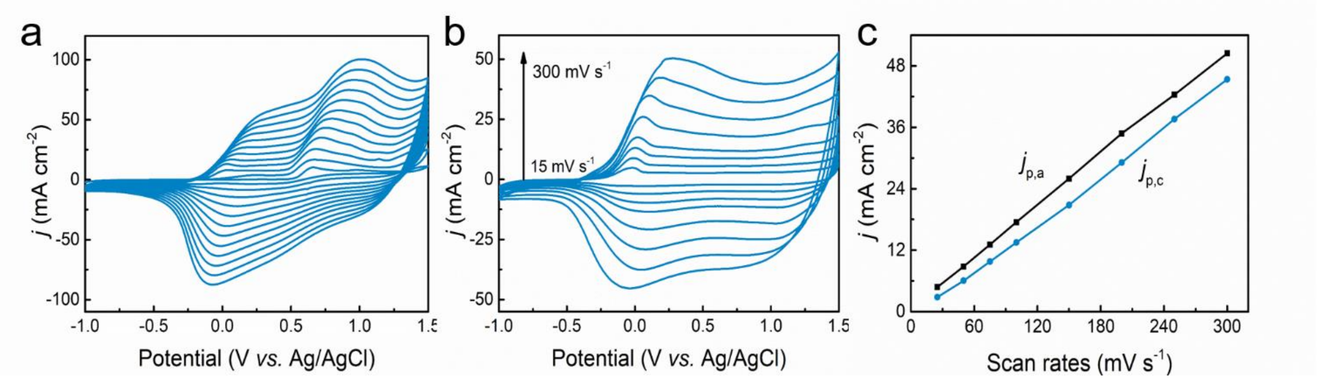


Figure 2. Electrochemical properties of poly(PEP). (a) CVs of PEP (0.05 mol L^{-1}) in ACN-Bu_4NPF_6 (0.1 mol L^{-1}) solution at the potential scan rate of 100 mV s^{-1}. (b) CVs of poly(PEP) in monomer-free ACN-Bu_4NPF_6 (0.1 mol L^{-1}) solution, potential scan rates: 25 ~ 300 mV s^{-1}. (c) plots of redox peak current densities as a function of potential scan rates.

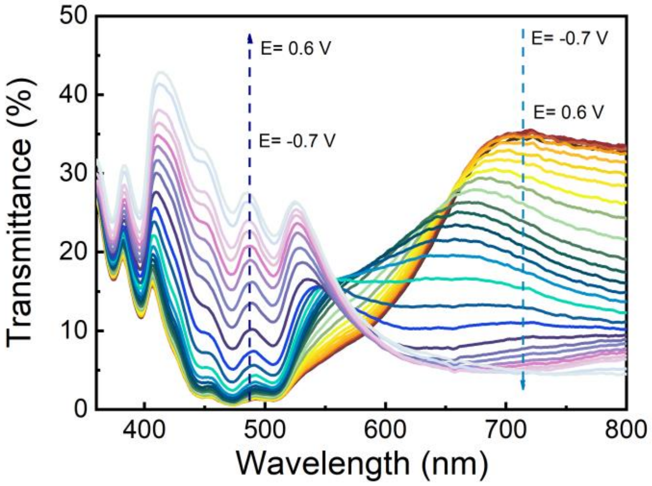


Figure 3. Electrochromic properties of poly(PEP). The transmission spectra of poly(PEP) film from -0.70 V to 0.60 V.

Followed by one-step Stille coupling of compounds 4 and 6, the desired monomer PEP is obtained with a yield of 20%. PEP exhibits high solubility in common organic solvents, such as dichloromethane (DCM) and acetonitrile (ACN). Finally, the poly(PEP) is electrochemical polymerized in 0.1 mol L^{-1} ACN-Bu_4NPF_6 at room temperature. Compound 3 and 6 are prepared by previous literature procedure [30, 32].

Figure 2a displays the recorded cyclic voltammograms (CVs) during the electrochemical polymerization of PEP. The onset oxidation potential of PEP is 0.56 V according to the first cycle of CVs in Figure 2a [30, 33, 34]. The ever-increasing redox peak current densities means that the polymer is continuously deposited on the electrode surface. Meanwhile, these broad redox peaks of the polymer that observed during the polymerization process, could be ascribed to the wide distribution of polymer chain length and the mutual transition of conductive species in different states [30, 33-35].

To further investigate the electrochemical behaviour of poly(PEP), a polymer-coated ITO electrode is studied by cyclic voltammetry in monomer-free ACN-Bu_4NPF_6 (0.1 mol L^{-1}), as shown in in Figure 2b. Since the current densities of anodic peaks ($j_{p,a}$) and cathodic peaks ($j_{p,c}$) are linearly proportional to the scan rate (Figure 2c), it could be concluded that the polymer adheres to the working electrode surface and the redox process of poly(PEP) is non-diffusion controlled [36-38].

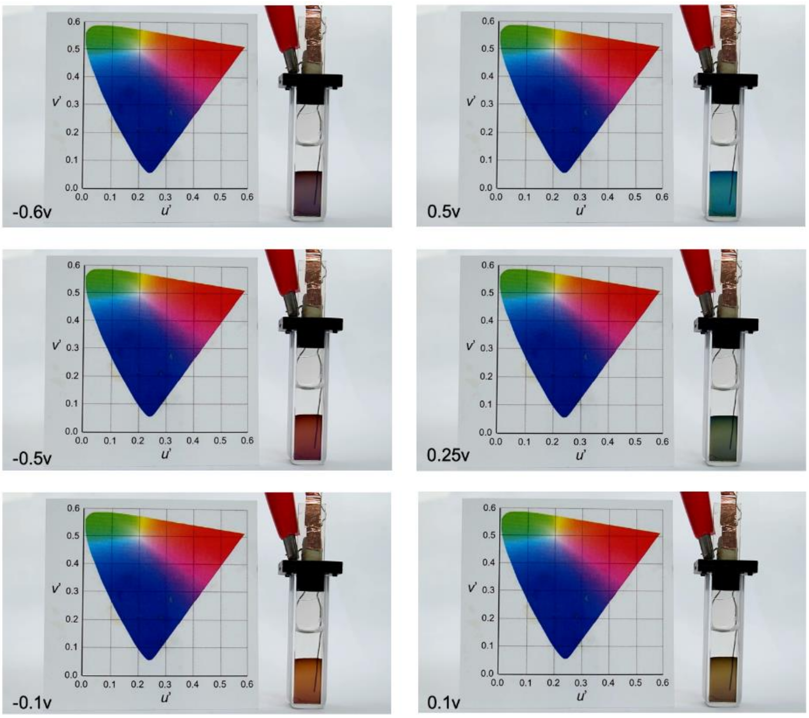


Figure 4. Photos for the poly(PEP) film with different applied voltages: -0.6 V, -0.5 V, -0.1 V, 0.10 V, 0.25 V, 0.5 V.

Table 1. CIE L*ab values and corresponding color swatches as a function of applied voltages: -0.60 V, -0.50 V, -0.10 V, 0.10 V, 0.25 V, 0.50 V.

E (V)	L*	a	b	Color
-0.60	29.2	19.5	-2.6	🟪
-0.50	34.5	26.9	30.6	🟫
-0.10	39.8	23.7	36.3	🟫
0.10	44.1	17.2	36.9	🟫
0.25	41.3	-3.1	6.4	⬛
0.50	47.8	-17.3	-23.9	🟦

The doping degree of the electrochromic polymer significantly depends on the applied external voltage, which results in variations in the energy band and optical absorption as well as the obvious switching of visible colours. The transmission spectra of the ploy(PEP) film are measured under different applied potentials ranging from -0.7 V to 0.6 V, as shown in Figure 3. As the applied potential gradually increases from -0.7 V to 0.6 V, the transmittance of ploy(PEP) dramatically changes, accompanied by changes in the polymer colour to purple, red, orange, yellowish-green, green, and blue (Figure 4). This colour tuning process may originate from the decreased valence intensity of the π-π* transition and the formation of polaronic and bio-polaronic carriers on the polymer backbone [14, 18, 25, 30, 38], which deform the film structure as the potential is changed. The final manifestation is that as the applied potential changes, the colour of the film changes continuously (Table S1). To avoid collimation error, the colour change of the film is further verified based on the spectrum colour model. The spectral data corresponding to six different potentials shown in Figure 4 are extracted, and their corresponding CIE L*ab values and colors are calculated as shown in Table 1. Obviously, the calculated color from the corresponding potential curve is in good agreement with the observed color in Figure 4, which further indicates that poly(PEP) film could be regarded as a real single polymeric template-based multicolor electrochromic material.

More importantly, the colour of this single polymeric template-based multi-colour electrochromic film is reversible and tuneable. However, stability remains a challenge. After 50 full cycles covering all the voltages from -0.7 V to 0.6 V, the transmission peak of the poly(PEP) film broadens and moves towards a longer wavelength, i.e., a redshift occurs, and the characteristic peak disappears as the potential is changed (Figure S5). Meanwhile, the colour of the film tends to change only between purple and light blue (Table 2). This effect comes from the fact that the structure of the electrochromic film is stable at a high potential and unstable at a low potential. As shown in Figure S6, with the applied potential changing from -0.60 V to 0.50 V, the morphology of the poly(PEP) film changes from aggregated clusters to porous flakes and finally becomes a relatively uniform and smooth film. In other words, the film at high potentials is denser than that at low potentials. When the potential is low, the film is loose and has poor stability, which leads to exfoliation of part of the film material from the electrode and deteriorates the stability of the electrochromic devices. In principle, this issue may be addressed by selecting different conjugated polymer components (modulating the polymerization potential) as well as using in situ polymerization to construct all-solid electrochromic devices.

4. CONCLUSION

In summary, a single polymeric template-based organic electrochromic material poly(PEP) is synthesized, which shows multi-color reversible tuning capability. As an effective approach to the dynamic manipulation of colors, the prepared single polymeric template-based electrochromic material is promising for a variety of low-cost optoelectronic and environmentally friendly applications.

ACKNOWLEDGEMENTS
We are grateful for the valuable discussion and suggestion from Dr. Alec Talin.

SUPPORTING INFORMATION

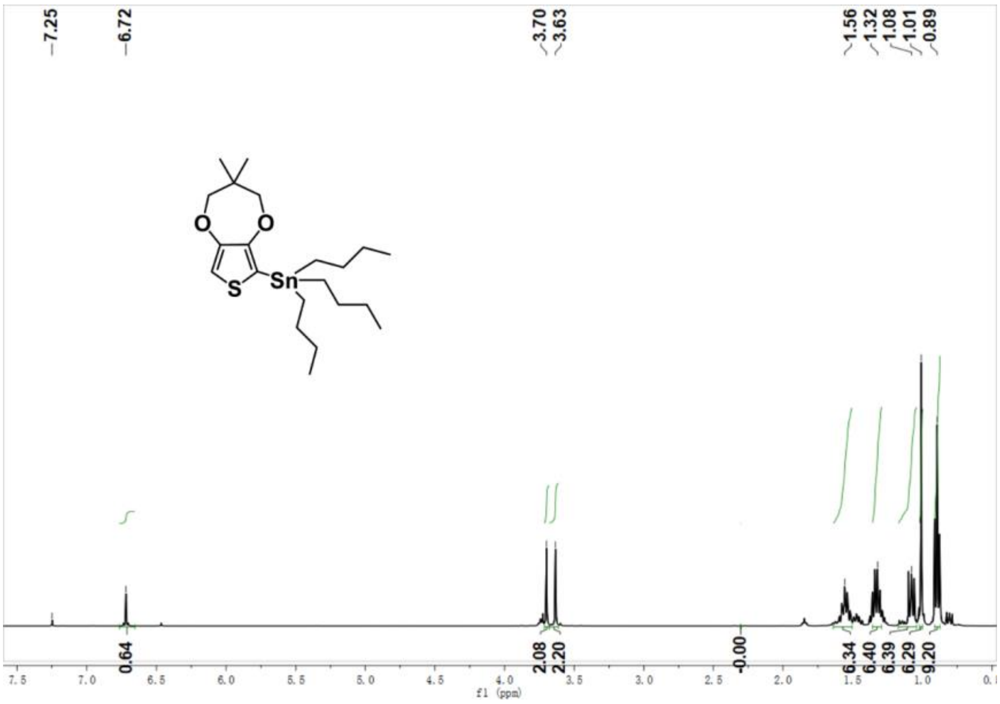


Figure S1 ^{1}H NMR spectrum of Compound 4 in $CDCl_3$.

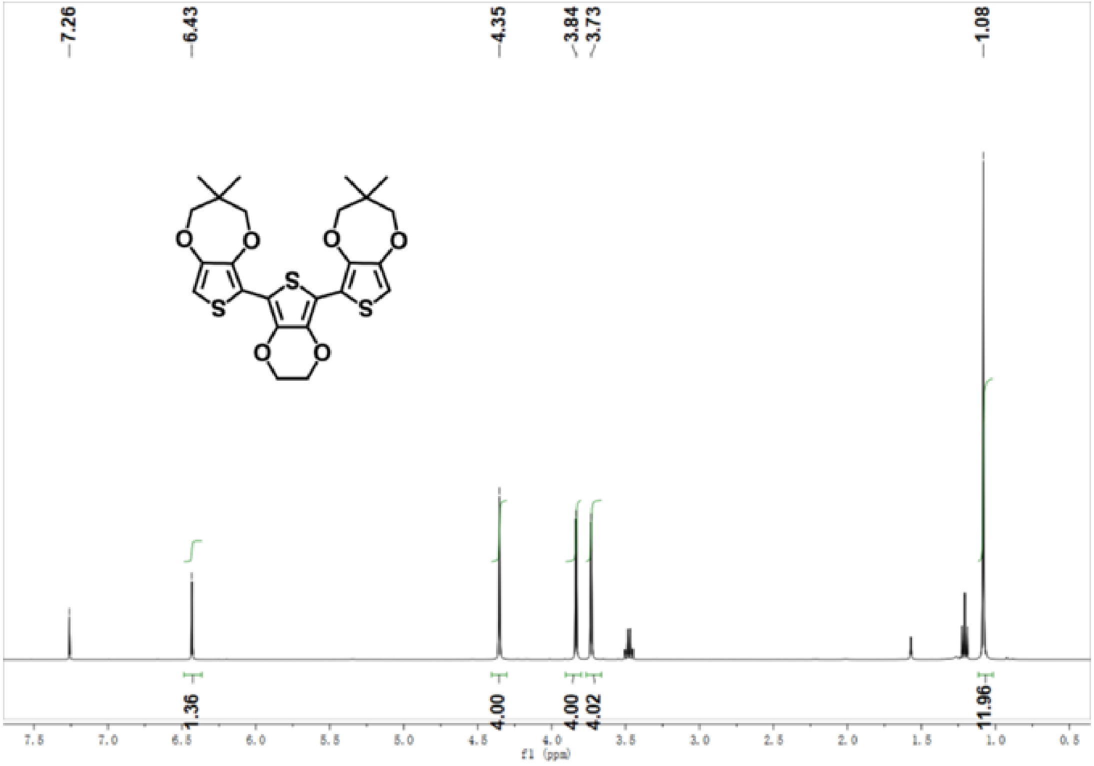


Figure S2 ^{1}H NMR spectrum of PEP in $CDCl_3$.

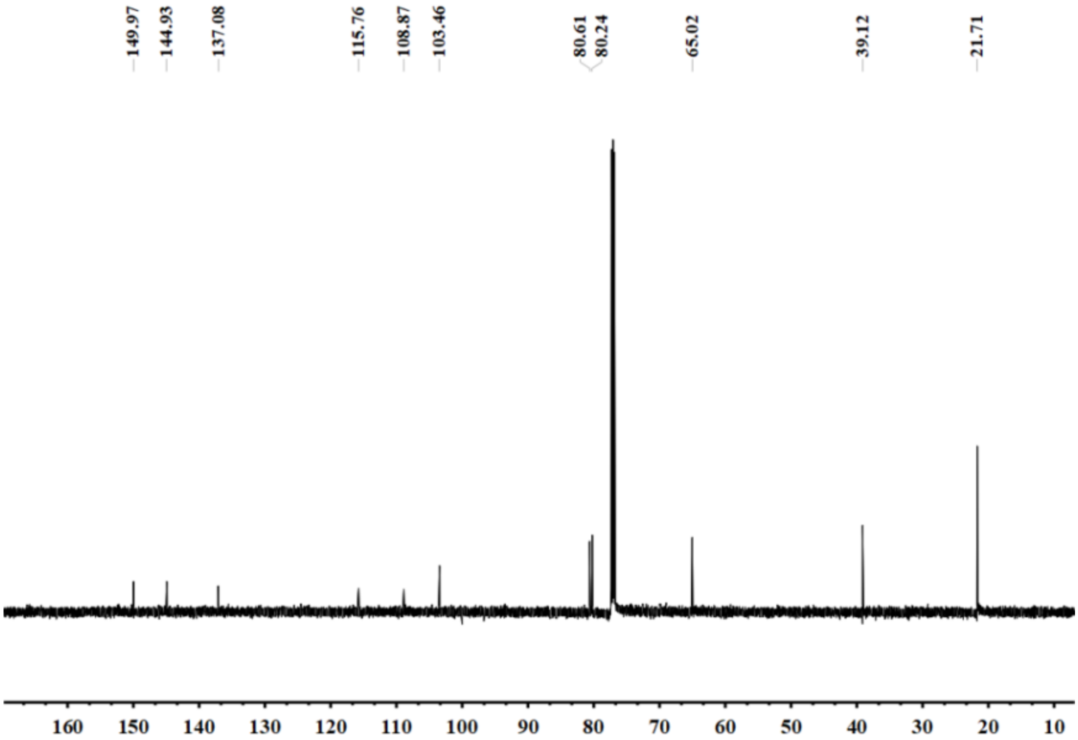
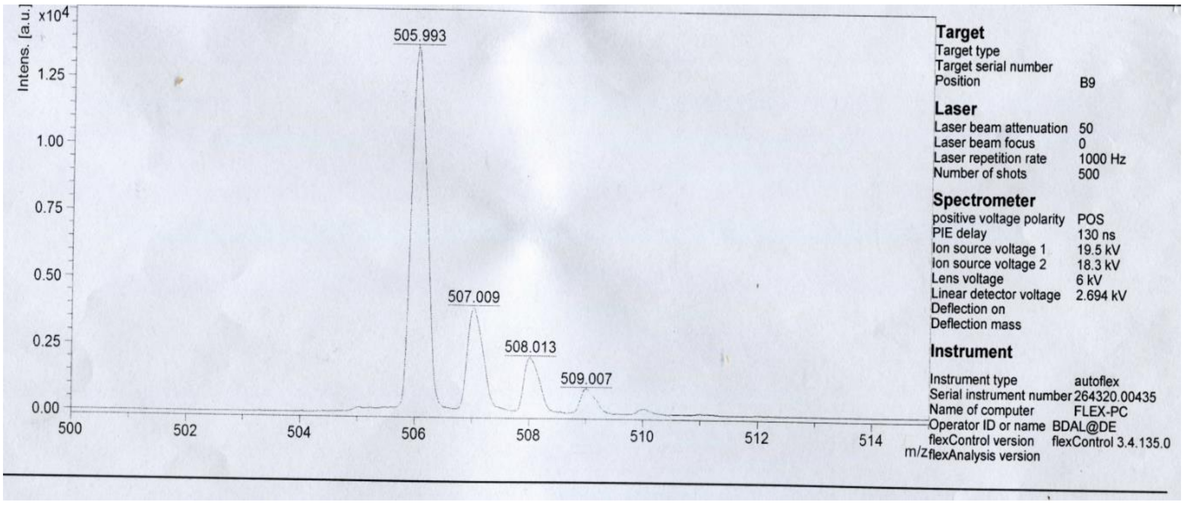


Figure S3 ^{13}C NMR spectrum of PEP in CDCl$_3$.



```
Target
Target type
Target serial number
Position                    B9
Laser
Laser beam attenuation      50
Laser beam focus            0
Laser repetition rate       1000 Hz
Number of shots             500
Spectrometer
positive voltage polarity   POS
PIE delay                   130 ns
Ion source voltage 1        19.5 kV
Ion source voltage 2        18.3 kV
Lens voltage                6 kV
Linear detector voltage     2.694 kV
Deflection on
Deflection mass
Instrument
Instrument type             autoflex
Serial instrument number    264320.00435
Name of computer            FLEX-PC
Operator ID or name         BDAL@DE
flexControl version         flexControl 3.4.135.0
flexAnalysis version
```

Figure S4 HRMS result of PEP.

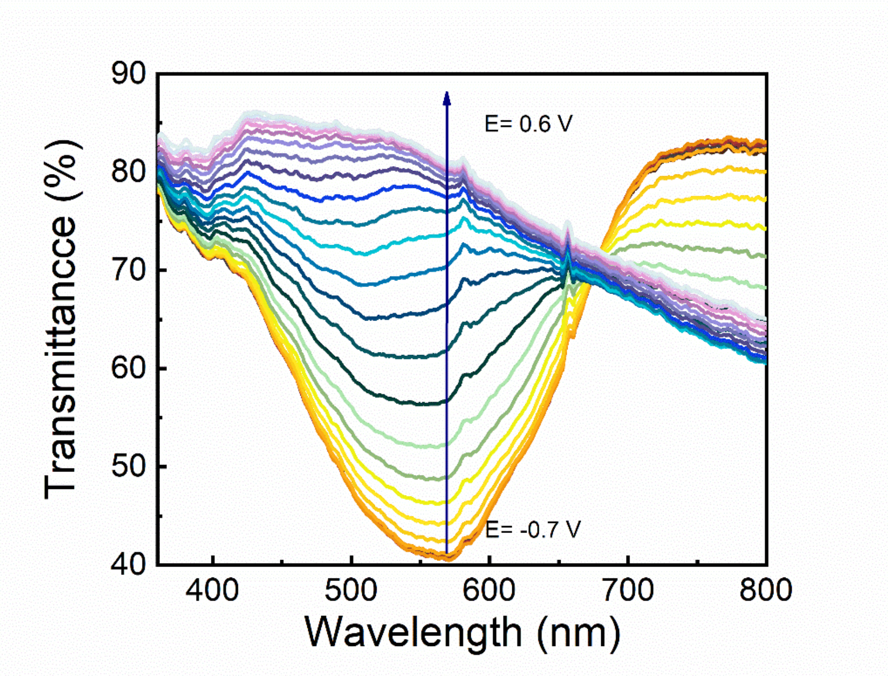


Figure S5 The transmission spectra of poly(PEP) film from -0.70 V to 0.60 V, after 50 cycles.

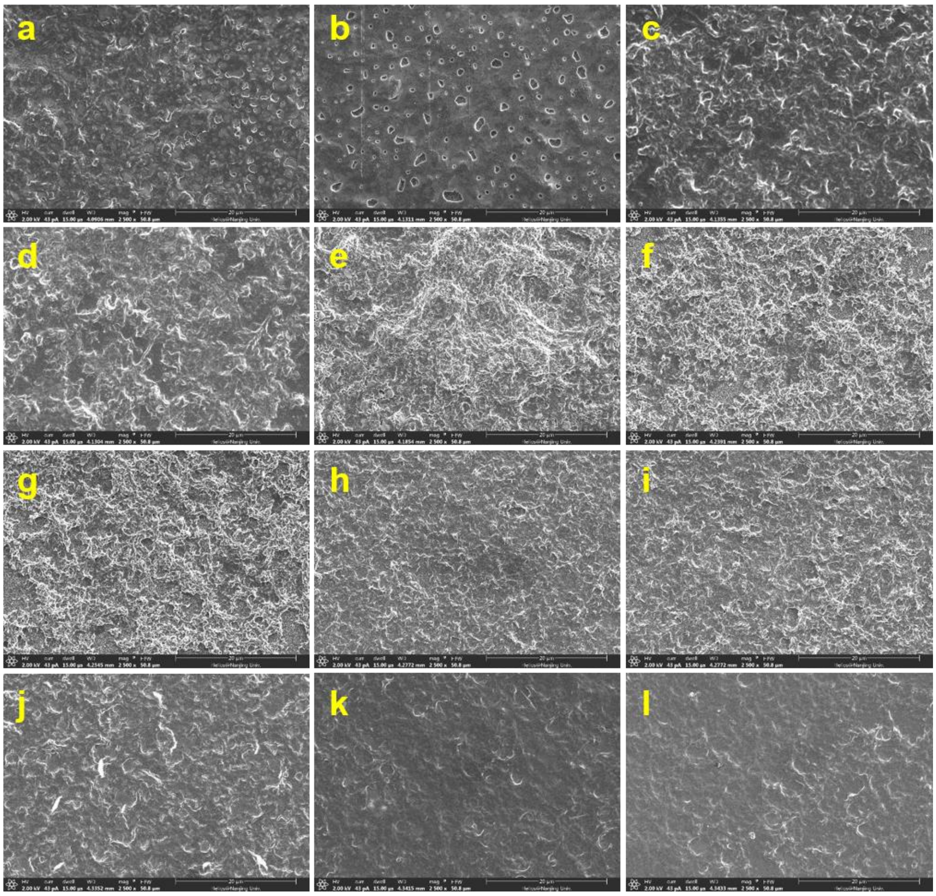
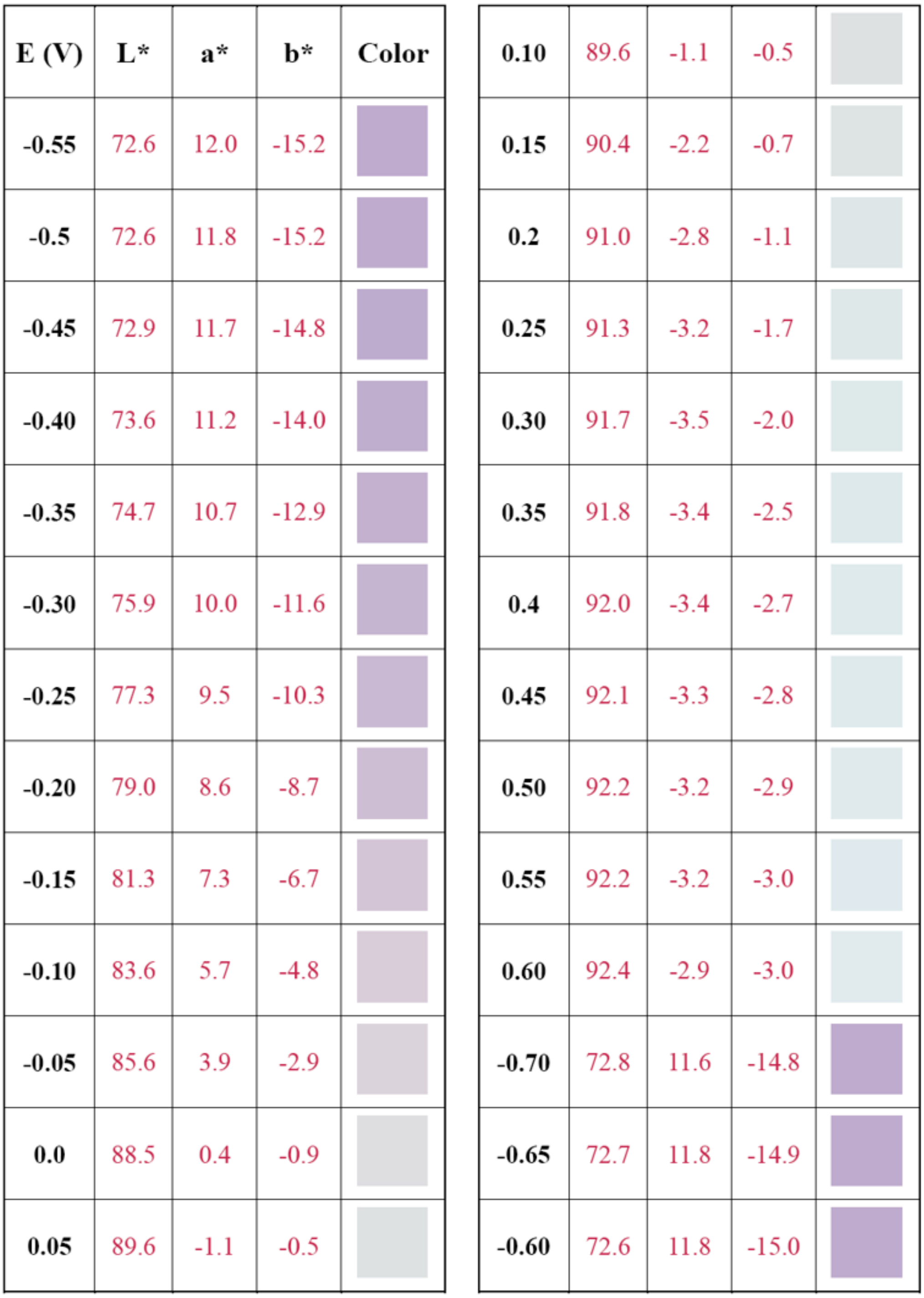


Figure S6 SEM of poly(PEP) films under different potentials from a to l (from -0.60 V to 0.50 V with a step of 0.10 V).

Table S1. CIE L*ab values and corresponding color swatches as a function of applied voltages from -0.70 V to 0.60 V with a step of 0.05 V.

E (V)	L*	a	b	Color
-0.55	34.4	26.7	29.4	🟫
-0.5	34.5	26.9	30.6	🟫
-0.45	34.6	27.1	30.3	🟫
-0.40	34.9	27.1	30.9	🟫
-0.35	35.3	27.0	31.7	🟫
-0.30	35.6	26.8	31.9	🟫
-0.25	36.2	26.4	33.1	🟫
-0.20	37.6	25.5	34.1	🟫
-0.15	38.7	24.6	35.7	🟫
-0.10	39.8	23.7	36.3	🟫
-0.05	41.4	22.4	37.9	🟫
0.0	43.0	20.6	39.1	🟫
0.05	43.8	19.3	38.4	🟫
0.10	44.1	17.2	36.9	🟫
0.15	43.6	7.4	24.4	🟫
0.2	42.3	2.0	15.4	🟫
0.25	41.3	-3.1	6.4	⬛
0.30	40.9	-9.1	-2.8	⬛
0.35	44.1	-18.7	-14.7	🟦
0.4	46.4	-19.8	-20.2	🟦
0.45	47.6	-18.1	-23.2	🟦
0.50	47.8	-17.3	-23.9	🟦
0.55	48.0	-16.4	-25.5	🟦
0.60	47.8	-16.6	-25.8	🟦
-0.70	32.8	16.1	-7.2	🟪
-0.65	30.7	18.4	-4.7	🟪
-0.60	29.2	19.5	-2.6	🟪

Table S2 CIE L*ab values and corresponding color swatches as a function of applied voltages from -0.70 V to 0.60 V with a step of 0.05 V, after 50 cycles.



E (V)	L*	a*	b*	Color
-0.55	72.6	12.0	-15.2	🟪
-0.5	72.6	11.8	-15.2	🟪
-0.45	72.9	11.7	-14.8	🟪
-0.40	73.6	11.2	-14.0	🟪
-0.35	74.7	10.7	-12.9	🟪
-0.30	75.9	10.0	-11.6	🟪
-0.25	77.3	9.5	-10.3	🟪
-0.20	79.0	8.6	-8.7	🟪
-0.15	81.3	7.3	-6.7	🟪
-0.10	83.6	5.7	-4.8	🟪
-0.05	85.6	3.9	-2.9	🟪
0.0	88.5	0.4	-0.9	⬜
0.05	89.6	-1.1	-0.5	⬜
0.10	89.6	-1.1	-0.5	⬜
0.15	90.4	-2.2	-0.7	⬜
0.2	91.0	-2.8	-1.1	⬜
0.25	91.3	-3.2	-1.7	⬜
0.30	91.7	-3.5	-2.0	⬜
0.35	91.8	-3.4	-2.5	⬜
0.4	92.0	-3.4	-2.7	⬜
0.45	92.1	-3.3	-2.8	⬜
0.50	92.2	-3.2	-2.9	⬜
0.55	92.2	-3.2	-3.0	⬜
0.60	92.4	-2.9	-3.0	⬜
-0.70	72.8	11.6	-14.8	🟪
-0.65	72.7	11.8	-14.9	🟪
-0.60	72.6	11.8	-15.0	🟪

References

1. S. K. Deb, J. A. Chopoorian, *J Appl Phys.,* 37 (1966) 4818.
2. S. K. Deb, *Appl Opt.,* 8 (1969) 192.
3. A. A. Argun, P. H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto,

D. B. Tanner, A. G. Macdiarmid and J. R. Reynolds, *Chem Mater.,* 16 (2004) 4401.

4. M. T. Otley, F. A. Alamer, Y. M. Zhu, A. Singhaviranon, X. Z. Zhang, M. F. Li, A. Kumar and G. A. Sotzing, *ACS Appl Mater Interfaces,* 6 (2014) 1734.
5. A. Kumar, D. M. Welsh, M. C. Morvant, F. Piroux, K. A. Abboud and J. R. Reynolds, *Chem Mater.,*10 (1998) 896.
6. B. GÉLinas, D. Das and D. Rochefort, *ACS Appl Mater Interfaces,* 9 (2017) 28726.
7. R. J. Mortimer, A. L. Dyer and J. R. Reynolds, *Displays,* 27 (2006) 2.
8. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv Mater.,* 12 (2000) 481.
9. G. Sonmez, H. Meng and F. Wudl, *Chem Mater.,* 16 (2004) 574.
10. L. Groenendaal, G. Zotti, P. H. Aubert, S. M. Waybright and J. R. Reynolds, *Adv Mater.,* 15 (2003) 855.
11. N. C. Davy, M. Sezen-Edmonds, J. Gao, X. Lin, A. Liu, N. Yao, A. Kahn and Y. L. Loo, *Nat Energy,* 2 (2017) 17104.
12. A. L. S. Eh, A. W. M. Tan, X. Cheng, S. Magdassi and P. S. Lee, *Energy Technology,* 6 (2018) 33.
13. J. Z. He, S. Mukherjee, X. R. Zhu, L. Y. You, B. W. Boudouris and J. G. Mei, *ACS Appl Mater Interfaces,* 10 (2018)18956.
14. T. Dey, M. A. Invernale, Y. Ding, Z. Buyukmumcu and G. A. Sotzing, *Macromolecules,* 44 (2011) 2415.
15. Q. Pei, G. Zuccarello, M. Ahlskog and O. Inganäs, *Polymer,* 35 (1994) 1347.
16. G. Sonmez, F. Wudl, *J Mater Chem.,* 15 (2005) 20.
17. P. Tehrani, L. O. Hennerdal, A. L. Dyer and J. R. Reynolds, *J Mater Chem.,* 19 (2009) 1799.
18. P. M. Beaujuge, J. R. Reynolds, *Chem Rev.,* 110 (2010) 268.
19. L. Beverina, G. A. Pagani and M. Sassi, *Chem Commun.,* 50 (2014) 5413.
20. B. Scrosati, Applications of Electroactive Polymers, London: Chapman & Hall, 1993.
21. P. R. Somani, M. S. Radhakrishnan, *Mater Chem Phys.,* 77 (2003) 117.
22. J .Kim, J. You, B. Kim, T. Park and E. Kim, *Adv Mater.,* 23 (2011) 4168.
23. D. Baeriswyl, D. K. Campbell, G. C. Clark, G Harbeke, P. K. Kahol, H. Kiess, S. Mazumdar, M. Mechring and W. Rehwald, Conjugated Conducting Polymers, Springer Science & Business Media, 2012.
24. F. A. Alamer, M. T. Otley, Y. Ding and G. A. Sotzing, *Adv Mater.,* 25 (2013) 6256.
25. E. Karabiyik, E. Sefer, F. Baycan Koyuncu, M. Tonga, E. ÖZdemir and S. Koyuncu, *Macromolecules,* 47 (2014) 8578.
26. H. Oh, D. G. Seo, T. Y. Yun, C. Y. Kim and H. C. Moon, *ACS Appl Mater Interface,* 9 (2017) 7658.
27. Z. Wan, J. Zeng, H. Li, P. Liu and W. Deng, *Macromol Rapid Commun.,* 39 (2018) 1700886.
28. M. Lahav, M. E. van der Boom, *Adv Mater.,* 30 (2018) 1706641.
29. J. A. Kerszulis, K. E. Johnson, M. Kuepfert, D. Khoshabo, A. L. Dyer and J. R. Reynolds, *J Mater Chem C.,* 3 (2015) 3211.
30. B. Y. Lu, S. J. Zhen, S. M. Zhang, J. K. Xu and G. Zhao, *Polym Chem.,* 5 (2014) 4896.
31. T. Xu, E. C. Walter, A. Agrawal, C. Bohn, J. Velmurugan; W. Q. Zhu, H. J. Lezec and A. A. Talin, *Nat Commun.,* 7 (2016) 10479.
32. D. M. Welsh, A. Kumar, E. W. Meijer and J. R. Reynolds, *Adv Mater.,* 11 (1999) 1379.
33. S. L. Ming, S. J. Zhen, K. W. Lin, L. Zhao, J. K. Xu and B. Y. Lu, *ACS Appl Mater Interfaces,* 7 (2015) 11089.
34. S. L. Ming, S. J. Zhen, X. M. Liu, K. W. Li n, H. T. Liu, Y. Zhao, B. Y. Lu and J. K. Xu, *Polym Chem.,* 6 (2015) 8248.
35. A. Elschner, S. Kirchmeyer, W. Lovenich, U. Merker and K. Reuter, PEDOT: Principles and Applications of an Intrinsically Conductive Polymer, CRC Press, 2010.
36. G. Sönmez, I. Schwendeman, P. Schottland, K. Zong and J. R. Reynolds, *Macromolecules,* 36 (2003) 639.
37. S. Toksabay, S. O. Hacioglu, N. A. Unlu, A. Cirpan and L. Toppare, *Polymer.,* 55 (2014) 3093.

38. G. M. Nie, L. Wang and C. L. Liu, *J Mater Chem C.,* 3 (2015) 11318.