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Boosting the Performance of Organic Cathodes through Structure Tuning

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The decisive factor to realize high-capacity rechargeable batteries is the cathode. Since the experimental capacity of inorganic cathodes is usually less than 200 mAh g⁻¹, searching new cathode materials to boost the capacity is highly desirable. Here, we design and synthesize two novel organic cathodes, poly(pyrene-4,5,9,10-tetraone) (PPTO) and poly(2,7-ethynylpyrene-4,5,9,10-tetraone) (PEPTO), based on the highly redox-active pyrene-4,5,9,10-tetraone. Due to their four Li⁺ ions intake characteristics, both cathodes show a large reversible capacity of 234 & 244 mAh g⁻¹ and a high energy density up to 530 & 507 Wh kg⁻¹, respectively. In particular, benefiting from the enhanced conjugation and planarity, PEPTO with the addition of a carbon-carbon triple bond (C≡C) delivers a significantly-improved rate stability at high current densities and an excellent capacity retention of 110 mAhg⁻¹ after 1000 cycles (at 800 mA g⁻¹). Our approach could provide an effective strategy to prepare new organic cathodes toward the next-generation of high stability and high energy density organic batteries through structure tuning.

Introduction

Organic redox-active materials have been demonstrated as suitable electrodes for advanced rechargeable batteries due to their structural diversity, reasonable sustainability, tunable properties, and possible high capacity associating with high energy density.¹⁻⁶ However, most of these materials encounter serious dissolution issue, causing sharp deterioration in cycling

and rate stability.⁷ Various strategies have been proposed to suppress this problem.⁸ The most common approach is to generate their enolate forms (-OM, M=Li⁺, Na⁺ & K⁺).⁹⁻¹³ Unfortunately, such formations will cause reduced energy densities due to the relatively lower operating voltages of organic salts. Recently, novel ideas have been demonstrated to realize highly-performed batteries with better stability. For example, the use of organic redox compounds with extended structures and rigid frameworks has been proven to be an effective solution.¹⁴⁻¹⁸ In addition, the introduction of sulfur (S) atoms or electron withdrawing groups (e.g. -F, -CN & -SO₃Na) can lead to enhanced stability and increased operating voltage.^{16, 19-21} Very recently, new organic materials with redox-active centers such as C=N,²² C=S²³ and N=N²⁴ also show greatly-improved redox ability and electronic conductivity. Although these approaches deliver several promising results, the target to achieve organic rechargeable batteries with high energy density, stable cycling, and steady rate behavior remains a big challenge.

Since the decisive factor to realize high-performance organic batteries is the cathode, it is necessary to design new organic cathode materials with multi-electron redox ability and high stability. The reported demonstrations on organic cathodes are mainly focused on redox stable quinones due to their high energy density and good electronic stability.²⁵⁻³¹ Particularly, pyrene-4,5,9,10-tetraone (PTO), which can achieve full utilization of its carbonyl groups, is so far the only reported single monomer that has a unique characteristic of four Li⁺ intake ability above 1.5 V.³² Due to such a superior multi-electron redox capability, the designed PTO has an extraordinary high theoretical capacity. The full utilization of the redox centers in PTO is attributed to the stable highest occupied molecular orbital (HOMO) and the aromaticity upon reduction to form the tetravalent anion PTO⁴⁻.³² Nevertheless, the serious dissolution behavior limits the direct application of PTO in metal-ion shuttling organic batteries. Although such a behavior could be suppressed by polymerization or functionalization,^{27, 33, 34} less effort has been input to understand the influence of molecular structures and the

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effect of planarity on the stability of redox-active polymer cathodes. Such a gap strongly encourages us to address this issue through developing new stable organic cathodes with high energy densities via the perspective of structure designing and tailoring.

Herein, we initiate an innovative study by developing two novel organic cathodes. The selection of a suitable redox-active building block is considered from the viewpoints of capacity storage, operating voltage, and electronic stability. Since PTO is an excellent multi-redox-active organic model that can fully utilize its redox centers with a high operating voltage, we believe that two new polymers (PPTO and PEPTO) with PTO as the building block should have improved performance in

electrochemistry. In fact, our results clearly indicate that the as-prepared PPTO and PEPTO can be acted as cathode materials to deliver a high reversible capacity with a good cycling. More importantly, we found that the connection unit between two neighboring PTOs has a strong effect on the conjugation and planarity of the as-prepared polymers, which provides us an opportunity to tune the stability, capacity and energy density of organic cathodes. Especially, the replacement of a single C-C bond (in PPTO) with a carbon-carbon triple bond (in PEPTO) could greatly enhance the performance of organic cathodes. These results were further supported by density functional theory (DFT) calculations.

Scheme 1. (A) Design and synthesis of redox-active PPTO and PEPTO cathode materials. (B) and (C) Proposed reaction mechanisms for PPTO and PEPTO cathodes.

Results and Discussion

2,7-Dibromo-pyrene-4,5,9,10-tetraone (1) was prepared according to the reported procedures.³⁵ However, directly performing coupling reaction with compound 1 faces two issues: a) the degree of polymerization would be extremely small due to the poor solubility of 1; and b) the ortho-diketones might deactivate the catalyst during the coupling reaction through chelating interaction.³⁶ Therefore, in order to avoid these problems, we adopted a protection-deprotection strategy to prepare PEPTO and PPTO (Scheme 1A). Compound 1 was transformed into the tetraone-protected precursor 2 in a refluxing ethylene glycol solution with the catalysis of TsOH.H₂O. PPTO was successfully synthesized in a yield of 38% by hydrolyzing the desired product obtained through a nickel-catalytic self-polymerization of 2.³⁷ Following the same strategy, PEPTO was obtained by hydrolyzing the desired coupling product, which was made from 2 and

bis(trimethylstannyl)acetylene in a yield of 76%.³⁸ The detailed synthesis procedures of PPTO and PEPTO as well as their characterizations are provided in the supporting information (experimental section). Benefiting from four redox-active carbonyl groups on pyrene cores,³² PPTO and PEPTO are expected to reversibly lithiate and delithiate four lithium-ions during the discharge-charge process (Scheme 1B-C). Additionally, the formation of Li₄PPTO and Li₄PEPTO during the reduction can stabilize the reduced carbonyl groups.^{32, 33}

The molecular structures of PPTO and PEPTO were also examined by density functional theory (DFT) (B3LYP/6-31G*^{39, 40}). To simplify the calculation, PEPTO and PPTO trimers were selected and optimized (Figure 1A-B). Subsequent frequency analysis was performed to assure that the optimized structures were in stable states. Consistent with our assumption, the planarity of PEPTO is greatly enhanced after the introduction of triple bonds (C≡C). As depicted from the side view of the trimers, the dihedral angle between the adjacent PTO unit is ca. 34° (Figure 1C), while that for PEPTO is zero (Figure 1D). For

this reason, PEPTO with an enhanced conjugation is anticipated to deliver better electrochemical stability.

Figure 1. The optimized molecular structure of PPTO trimer, top view (A) and side view (C). The optimized molecular structure of PEPTO trimer, top view (B) and side view (D). (E) FTIR spectra of compound 2, PPTO and PEPTO. (F) TGA profiles of PPTO and PEPTO under a nitrogen atmosphere.

The chemical structure of **2** was confirmed by ¹HNMR, ¹³CNMR and HRMS (Figure S1-S3). Due to their poor solubility, the structures of PPTO and PEPTO can only be confirmed by FTIR and elemental analysis (EA). As shown in Figure 1E, compound **2** displays apparent multiple peaks at ~2947 cm⁻¹, which can be attributed to the -CH₂ group. No typical carbonyl (C=O) peaks can be observed at ~1700 cm⁻¹, indicating the successful protection of carbonyl groups. In contrast, the -CH₂ peaks at ~2900 cm⁻¹ disappear for both as-prepared PPTO and PEPTO. Moreover, two strong peaks at 1683 cm⁻¹ and 1678 cm⁻¹ for both PPTO and PEPTO reappear, suggesting the recovery of C=O functional groups after deprotection. EA was also conducted to further confirm the elemental composition of PPTO and PEPTO (refer to the supporting information). In addition, PPTO and PEPTO show good thermal stabilities as examined by thermal gravimetric analysis (TGA) (Figure 1F). Both compounds are thermally stable up to 400 °C and 360 °C, respectively (indicated by the 10% weight loss). As shown in Figure S4A-B, the morphologies of as-prepared PPTO and PEPTO were characterized by high resolution scanning electron microscopy (HRSEM). They show nanostructured particles with average diameters in the ranges of 50-200 and 100-300 nm, respectively. After mixing both compounds with carbon nanotubes (CNTs) and binders, the electrodes with microporous structures are presented in Figure S5.

Electrochemical performances of PPTO and PEPTO were investigated by coin-type half-cell fabrications. As shown in the galvanostatic charge-discharge profiles (Figure 2A-B), PPTO and PEPTO deliver a large reversible capacity of 234 mAh g⁻¹ and 244 mAh g⁻¹ at the 1st charge, respectively. The different charge-discharge profiles of both compounds between the 1st

and the following cycles could be attributed to the oxidation of the electrolyte at a high voltage.⁴¹ Nevertheless, this side reaction could be inhibited at higher current densities.⁴¹ The specific capacities in the 2nd and 3rd cycles display insignificant deteriorations, indicating a good reversibility of PPTO and PEPTO. Both cathodes exhibit two pairs of sloping discharge plateaus at about 3.1-2.4 V, 2.4-1.7 V and 3.1-2.4 V, 2.5-1.9 V (vs. Li/Li⁺), generating an average operating voltage (discharge) of around 2.44 V for PPTO and 2.47 V for PEPTO (Table S1). Both plateaus indicate a two-stage redox behavior of each material.^{27, 32, 33} Figure 2C-D show the cycling performance of PPTO and PEPTO. The slightly higher CEs from PEPTO could be attributed to the oxidation of the electrolyte as previously mentioned. For PEPTO, the gap between the charge and discharge capacity needs a longer time (~10 cycles) to be digested as compared with PPTO. This might be attributed to the different sizes and morphologies of PPTO and PEPTO particles (Figure S4A-B). PPTO nanoparticles present uniform sizes and morphologies. For PEPTO with non-uniform morphologies, longer side reactions might be incurred between PEPTO surface and electrolyte during the electrochemical reaction. After 100 cycles, although the two cells show slight capacity deterioration, the reversible capacity of two materials could still be maintained at a high capacity of 161 mA h g⁻¹ for PPTO and 155 mAh g⁻¹ for PEPTO. Importantly, the Coulombic efficiency (CE) values of both polymers are as high as ~100%. To investigate the reaction mechanisms of both polymer-based electrodes, cyclic voltammetry (CV) analyses were conducted. Similar to the charge-discharge profiles, both PPTO and PEPTO encounter a two-step redox process between 3.5 and 1.5 V as revealed by the two pairs of distinct enolation

redox peaks at the carbonyl groups (Figure 2E-F): 2.8/3.2 V, 2.1/2.6 V for PPTO, and 2.9/3.0 V, 2.2/2.5 V for PEPTO, corresponding to two two-electron reactions at the four carbonyl groups. The results are in well accordance with the

cathode investigations on PTO based compounds^{27, 32, 33}. The CV profiles of both compounds in the following 2nd and 3rd cycles almost overlap, confirming the good reversibility of two polymer electrodes.

Figure 2. Electrochemical properties of PPTO and PEPTO cathodes between 3.5 and 1.5 V. Charge-discharge profiles of (A) PPTO and (B) PEPTO at 20 mA g⁻¹ (the initial three cycles). Cycling performance of (C) PPTO and (D) PEPTO at 20 mA g⁻¹. CV measurements of (E) PPTO and (F) PEPTO (the initial three cycles) at a scan rate of 0.2 mV s⁻¹. (G) Rate and long-term cycling stability of PPTO and PEPTO at various current densities.

The rate and long-term cycling stability of PPTO and PEPTO were further studied. It can be seen from the CEs that the side reaction originated from the electrolyte has been well inhibited at higher current densities. As shown in Figure 2G, PPTO delivers the reversible capacities of 230, 201, 161 and 22 mAh g⁻¹ at the current densities of 20, 50, 100 and 300 mA g⁻¹, respectively. Unfortunately, at relatively higher current densities of 500, 800 & 1500 mA g⁻¹ (the shadow pink zone),

the capacities of PPTO suddenly drop to infinitesimal values, revealing an extremely poor rate stability of PPTO under harsh conditions.^{42, 43} Nevertheless, when the current density was reset back to a small value (20 mA g⁻¹), PPTO could immediately recover a high value (96%) of its initial capacity (with respect to the average capacity at 20 mA g⁻¹). Due to the low rate stability, long-term cycling of PPTO was therefore conducted at only 100 mA g⁻¹, a high capacity of 97 mAh g⁻¹,

corresponding to a retention of 74% with regard to the 47th cycle (the 1st cycle when the current density was reset back), could still be obtained after 1000 cycles. As for PEPTO, the capacities of 249 and 200 mAh g⁻¹ delivered at low current densities of 20 and 50 mA g⁻¹ are very close to that of PPTO. In sharp contrast, at higher current densities from 100 mA g⁻¹ onward (the shadow pink zone), PEPTO shows a significantly-improved rate stability compared with PPTO. In detail, PEPTO delivers much higher capacities of 189, 176, 167 and 152 mAh g⁻¹ at 100, 300, 500 and 800 mA g⁻¹, respectively. Even at an extremely high current density of 1500 mA g⁻¹, PEPTO still delivers a capacity of 98 mAh g⁻¹. The capacity of PEPTO could recover 95% of its initial capacity (with respect to the average capacity at 20 mA g⁻¹). After 1000 cycles of continuous testing at a high current density of 800 mA g⁻¹, PEPTO could still achieve an excellent capacity of 110 mAh g⁻¹, corresponding to a high retention of 79% with respect to its 47th cycle. Moreover, PEPTO maintained a high CE of 99.80% at the 1000th cycle. The results of PEPTO exhibit much improvement in terms of operating voltage, cycling and rate stability as

compared with conventional cathode-active redox polymers, which deploy naphthalene diimide (NDI), perylene diimide (PDI) and pyromellitic diimides (PMDI) as the building units (Table S2).⁴³⁻⁴⁸

The superior rate stability of PEPTO (compared to PPTO) could also be observed from the specific capacity versus current density plots (Figure 3A). Especially, from 100 mA g⁻¹ onward (the shadow pink zone), PEPTO provides significantly-higher capacities comparing to PPTO. The energy density values delivered by PEPTO can therefore be expected to show great improvement as compared to those delivered by PPTO. As shown in Figure 3B, PEPTO provides Practical energy density and power density up to 507 Wh kg⁻¹ and 2961 W kg⁻¹, respectively. More importantly, the energy densities show insignificant deterioration at higher current densities (the shadow pink zone). In contrast, PPTO presents a much lower power density of 1622 W kg⁻¹. Although the Practical energy density could reach to a high value of 530 Wh kg⁻¹, the values show significant deterioration at higher current densities.

Figure 3. (A) Specific capacity versus current density plots of PPTO and PEPTO cathodes. (B) Practical energy density versus power density plots of PPTO and PEPTO cathodes. (C) Calculation of the energy levels (HOMO and LUMO) and optimized structures of PPTO and PEPTO trimers. (D) EIS comparison between PPTO and PEPTO, the frequency ranges from 100 kHz to 10 mHz.

To gain deeper insight into the relationship between the difference of rate stability and the electronic properties of PPTO and PEPTO, the energy levels of the HOMO and LUMO for the two compounds (their optimized trimer structures as models) were further investigated (Figure 3C). The LUMOs of PPTO (-3.94 eV) and PEPTO (-3.95 eV) trimers are very close, confirming the similar discharge behaviors of PPTO and PEPTO.³² Owing to the more effective conjugation of the planar PEPTO, the calculated bandgap (ΔE) for PEPTO trimer (2.65 eV) is much smaller than that of PPTO trimer (3.03 eV). A smaller ΔE can facilitate the electron and Li⁺ transfer in organic

batteries and therefore enhance the rate stability of PEPTO cathode.^{22, 49} Experimental electrochemical impedance spectroscopy (EIS) analysis was also conducted on the pristine states (before the 1st discharging) of PPTO and PEPTO fresh cells. As shown in Figure 3D, the Nyquist plots of PPTO and PEPTO cells are presented by the well-defined semicircles and straight lines. The charge transfer resistance (R_{ct}) of PEPTO is 210 Ω, which is much lower than that of PPTO (391 Ω). Evidently, a smaller R_{ct} resistance indicates a faster charge transfer capability.⁵⁰ This demonstration further confirmed that PEPTO is better than PPTO in terms of electronic

conductivity and lithiation kinetics. All results suggested that the introduction of C≡C bonds has effectively promoted the rate stability of PTO-based polyquinones. Thus, our hypothesis to improve the performance of organic cathodes from the perspective of structure designing and tuning has been well supported by this approach.

Conclusions

In conclusion, we have demonstrated an innovative strategy for the improved battery cathodes by designing two novel redox-active organic cathode materials. PPTO and PEPTO have been prepared and investigated with the aid of both computational and experimental analyses. The two cathodes (with respect to lithium anodes) demonstrate high specific capacities and energy densities. Benefiting from the enhanced conjugation and planarity, PEPTO with C≡C bonds as bridges shows effectively-improved rate and long-term stability, therefore delivering better performance at harsh conditions. Moreover, a reversible capacity (110 mAh g⁻¹) of PEPTO could still be retained after 1000 cycles with an excellent CE of 99.80%. This novel structure tuning strategy provides an alternative solution to develop new organic cathodes toward next-generation of high stability and energy density batteries.

Conflicts of interest

There are no conflicts to declare.

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References

1. T. B. Schon, B. T. McAllister, P.-F. Li and D. S. Seferos, *Chem. Soc. Rev.*, 2016, **45**, 6345-6404.
2. J. Kim, J. H. Kim and K. Ariga, *Joule*, 2017, **1**, 739.
3. Z. Song and H. Zhou, *Energy Environ. Sci.*, 2013, **6**, 2280-2301.
4. Y. Liang, Z. Tao and J. Chen, *Adv. Energy Mater.*, 2012, **2**, 742-769.
5. J. Xie and Q. Zhang, *J. Mater. Chem. A*, 2016, **4**, 7091-7106.
6. J. Xie, P. Gu and Q. Zhang, *ACS Energy Lett.*, 2017, **2**, 1985-1996.
7. S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka and U. S. Schubert, *Chem. Rev.*, 2016, **116**, 9438-9484.
8. Y. Zhang, J. Wang and S. N. Riduan, *J. Mater. Chem. A*, 2016, **4**, 14902-14914.
9. M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribière, P. Poizot and J.-M. Tarascon, *Nat. Mater.*, 2009, **8**, 120.
10. N. Ogihara, T. Yasuda, Y. Kishida, T. Ohsuna, K. Miyamoto and N. Ohba, *Angew. Chem. Int. Ed.*, 2014, **53**, 11467-11472.
11. M. Lee, J. Hong, J. Lopez, Y. Sun, D. Feng, K. Lim, W. C. Chueh, M. F. Toney, Y. Cui and Z. Bao, *Nat. Energy*, 2017, **2**, 861.
12. X. Chi, Y. Liang, F. Hao, Y. Zhang, J. Whiteley, H. Dong, P. Hu, S. Lee and Y. Yao, *Angew. Chem.*, 2018, **130**, 2660.
13. Q. Zhao, J. Wang, Y. Lu, Y. Li, G. Liang and J. Chen, *Angew. Chem. Int. Ed.*, 2016, **55**, 12528-12532.
14. D. J. Kim, K. R. Hermann, A. Prokofjevs, M. T. Otley, C. Pezzato, M. Owczarek and J. F. Stoddart, *J. Am. Chem. Soc.*, 2017, **139**, 6635-6643.
15. S. K. M. Nalluri, Z. Liu, Y. Wu, K. R. Hermann, A. Samanta, D. J. Kim, M. D. Krzyaniak, M. R. Wasielewski and J. F. Stoddart, *J. Am. Chem. Soc.*, 2016, **138**, 5968-5977.
16. (a) T. Ma, Q. Zhao, J. Wang, Z. Pan and J. Chen, *Angew. Chem. Int. Ed.*, 2016, **55**, 6428-6432; (b) Z. Luo, L. Liu, Q. Zhao, F. Li and J. Chen, *Angew. Chem. Int. Ed.*, 2017, **56**, 12561-12565; (c) Z.-Q. Lin, J. Xie, B. Zhang, J. Li, J.-N. Weng, R.-B. Song, X. Huang, H. Zhang, H. Li, Y. Liu, Z. J. Xu, W. Huang, Q. Zhang, *Nano Energy*, 2017, **41**, 117-127; (d) J. Xie, C.-E. Zhao, Z. Lin, P.-Y. Gu, Q. Zhang, *Chem. Asian J.*, 2016, **11**, 1489-1511; (e) J. Xie, X. Rui, P. Gu, J. Wu, Z. J. Xu, Q. Yan, Q. Zhang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 16932-16938.
17. (a) J. Xie, W. Chen, Z. Wang, K. C. W. Jie, M. Liu and Q. Zhang, *Chem. Asian J.*, 2017, **12**, 868-876; (b) J. Wu, X. Rui, G. Long, W. Chen, Q. Yan, Q. Zhang, *Angew. Chem. Int. Ed.*, 2015, **54**, 7354-7358; (c) J. Wu, X. Rui, C. Wang, W.-B. Pei, R. Lau, Q. Yan, Q. Zhang, *Adv. Energy Mater.*, 2015, **5**, 1402189.
18. M. Kolek, F. Otteny, P. Schmidt, C. Mück-Lichtenfeld, C. Einholz, J. Becking, E. Schleicher, M. Winter, P. Bieker and B. Esser, *Energy Environ. Sci.*, 2017, **10**, 2334-2341.
19. G. S. Vadehra, R. P. Maloney, M. A. Garcia-Garibay and B. Dunn, *Chem. Mater.*, 2014, **26**, 7151-7157.
20. W. Wan, H. Lee, X. Yu, C. Wang, K.-W. Nam, X.-Q. Yang and H. Zhou, *RSC Adv.*, 2014, **4**, 19878-19882.
21. C. Peng, G.-H. Ning, J. Su, G. Zhong, W. Tang, B. Tian, C. Su, D. Yu, L. Zu and J. Yang, *Nat. Energy*, 2017, **2**, 17074.
22. H. Zhao, J. Wang, Y. Zheng, J. Li, X. Han, G. He and Y. Du, *Angew. Chem.*, 2017, **129**, 15536-15540.
23. C. Luo, G.-L. Xu, X. Ji, S. Hou, L. Chen, F. Wang, J. Jiang, Z. Chen, Y. Ren and K. Amine, *Angew. Chem. Int. Ed.*, 2018, **57**, 2879.
24. B. Häupler, A. Wild and U. S. Schubert, *Adv. Energy Mater.*, 2015, **5**, 1402034.
25. Y. Wu, R. Zeng, J. Nan, D. Shu, Y. Qiu and S. L. Chou, *Adv. Energy Mater.*, 2017, **7**, 1700278.
26. Y. Liang, Y. Jing, S. Gheytani, K.-Y. Lee, P. Liu, A. Facchetti and Y. Yao, *Nat. Mater.*, 2017, **16**, 841-848.
27. J. E. Kwon, C.-S. Hyun, Y. J. Ryu, J. Lee, D. J. Min, M. J. Park, B.-K. An and S. Y. Park, *J. Mater. Chem. A*, 2018, **6**, 3134.
28. L.-B. Zhao, S.-T. Gao, R. He, W. Shen and M. Li, *ChemSusChem*, 2018, **11**, 1215.
29. J. Xie, Z. Wang, P. Gu, Y. Zhao, Z. J. Xu and Q. Zhang, *Sci. China Mater.*, 2016, **59**, 6-11.
30. J. Xie, Z. Wang, Z. J. Xu and Q. Zhang, *Adv. Energy Mater.*, 2018, 1703509. DOI: 10.1002/aenm.201703509

32. Y. Liang, P. Zhang and J. Chen, *Chem. Sci.*, 2013, **4**, 1330-1337.
33. T. Nokami, T. Matsuo, Y. Inatomi, N. Hojo, T. Tsukagoshi, H. Yoshizawa, A. Shimizu, H. Kuramoto, K. Komae and H. Tsuyama, *J. Am. Chem. Soc.*, 2012, **134**, 19694-19700.
34. A. Shimizu, H. Kuramoto, Y. Tsujii, T. Nokami, Y. Inatomi, N. Hojo, H. Suzuki and J.-i. Yoshida, *J. Power Sources*, 2014, **260**, 211-217.
35. S.-i. Kawano, M. Baumgarten, D. Chercka, V. Enkelmann and K. Müllen, *Chem. Commun.*, 2013, **49**, 5058-5060.
36. S. N. Keller, A. D. Bromby and T. C. Sutherland, *Eur. J. Org. Chem.*, 2017, **2017**, 3980-3985.
37. M. J. Jiang, X. Y. Li, L. T. Sun, X. L. Niu, Q. M. Liang, X. Q. Cai, J. C. Huang, J. Ling and Y. Q. Mo, *Chin. J. Polym. Sci.*, 2017, **35**, 1097-1109.
38. Y. Liu, L. Zhang, H. Lee, H. W. Wang, A. Santala, F. Liu, Y. Diao, A. L. Briseno and T. P. Russell, *Adv. Energy Mater.*, 2015, **5**, 1500195.
39. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
40. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
41. Z. Song, Y. Qian, T. Zhang, M. Otani and H. Zhou, *Adv. Sci.*, 2015, **2**, 1500124.
42. Z. Song, Y. Qian, X. Liu, T. Zhang, Y. Zhu, H. Yu, M. Otani and H. Zhou, *Energy Environ. Sci.*, 2014, **7**, 4077-4086.
43. Y. Meng, H. Wu, Y. Zhang and Z. Wei, *J. Mater. Chem. A*, 2014, **2**, 10842-10846.
44. P. Sharma, D. Damien, K. Nagarajan, M. M. Shaijumon and M. Hariharan, *J. Phys. Chem. Lett.*, 2013, **4**, 3192-3197.
45. F. Xu, H. Wang, J. Lin, X. Luo, S.-a. Cao and H. Yang, *J. Mater. Chem. A*, 2016, **4**, 11491-11497.
46. D. Tian, H.-Z. Zhang, D.-S. Zhang, Z. Chang, J. Han, X.-P. Gao and X.-H. Bu, *RSC Adv.*, 2014, **4**, 7506-7510.
47. H. Wu, K. Wang, Y. Meng, K. Lu and Z. Wei, *J. Mater. Chem. A*, 2013, **1**, 6366-6372.
48. H. Zhang, Y. Xie, X. Chen, T. Jia, W. Huang, S. Luo, Q. Hou, R. Zeng and Z. Sun, *J. Electrochem. Soc.*, 2017, **164**, A290-A294.
49. J. Lee, H. Kim and M. J. Park, *Chem. Mater.*, 2016, **28**, 2408-2416.
50. E. Talaie, P. Bonnick, X. Sun, Q. Pang, X. Liang and L. F. Nazar, *Chem. Mater.*, 2016, **29**, 90-105.