RESEARCH HIGHLIGHTS

Journal of Semiconductors
(2021) 42, 100202
doi: 10.1088/1674-4926/42/10/100202

n-Type acceptor–acceptor polymer semiconductors

Yongqiang Shi[1, †] and Liming Ding[2, †]

[1]College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China

[2]Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China

Citation: Y Q Shi and L M Ding, n-Type acceptor–acceptor polymer semiconductors[J]. *J. Semicond.*, 2021, 42(10), 100202. http://doi.org/10.1088/1674-4926/42/10/100202

Polymer semiconductors have aroused interests from both academic and industry due to their wide applications in electronic devices, such as organic thin-film transistors (OTFTs)[1], polymer solar cells (PSCs)[2–6], organic thermoelectrics (OTEs)[7–11], and perovskite solar cells (PVSCs)[12–14]. To date, great efforts have been devoted to developing p-type polymer semiconductors, while the development of n-type polymers lags far behind. In fact, n-type polymers are essential for organic electronic devices.

Currently, lots of n-type polymers are donor–acceptor (D–A) copolymers[15], however, the electron-rich donor units can lift both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), yielding p-type or ambipolar charge-transport characteristics. To inhibit hole injection and achieve unipolar electron-transport, acceptor–acceptor (A–A) combination could be a good strategy. For instance, Luscombe *et al.*[16] reported a NDI-based A–A homopolymer *via* Yamamoto coupling, however the polymer showed a low μ_e of 6×10^{-4} cm^2/(V·s) due to high steric hindrance of NDI unit. To reduce steric hindrance of NDI, thiophene-fused NDI derivative, naphtho[2,3-*b*:6,7-*b*′]-dithiophenediimide (NDTI), was designed by Takimiya *et al.* Subsequently, various n-type A–A polymer semiconductors (PNDTI-BBT-DP and PNB-TzDP) from NDTI were developed with high electron mobility and electrical conductivity, and were applied in OTFTs and OTEs (Fig. 1)[17–19]. Reichmanis *et al.* developed a thiazole-based A–A type polymer PDPP5DH-4Tz[20] by replacing the flanked thiophene units of DPP with thiazoles, and it presented unipolar charge-transport properties with μ_e of 0.067 cm^2/(V·s).

Among various electron-deficient units, bithiophene imide (BTI) has been proved to be an eminent unit for building n-type polymer semiconductors. Guo *et al.* developed a serious of highly electron-deficient semi-ladder BTI derivatives (BTIn) with up to 5 imide groups and 15 rings in a row, offering a remarkable platform for developing n-type polymer semiconductors[21]. Subsequently, they also synthesized bithiazole imide (BTzI)[22] and thiazolothienyl imide dimer (DTzTI)[23] electron-deficient units by replacing thiophene with thiazole to further push down the frontier molecular orbitals (FMOs) energy levels, as a result, both A–A type polymers PBTzI and PDTzTI (Fig. 1) showed unipolar n-type character in OTFTs. PDTzTI exhibited a remarkably high μ_e of 1.61 cm^2/(V·s). This polymer structure also favors to overcome Coulomb interaction in the doped state for OTEs. The doped PDTzTI presented good charge-generation, giving a remarkable electrical conductivity (σ) of 4.6 S/cm and a power factor (PF) of 7.6 μW/(m·K^2), much higher than those of NDI polymers[24]. Owing to its high electron mobility and well-matched energy levels, PDTzTI as electron-transport layer (ETL) in inverted PVSCs yielded a PCE of 20.8% [25]. Driven by the success of A–A type homopolymer PDTzTI, Guo *et al.* also developed a serious of A–A type homopolymers PBTIn (n = 1–5) (Fig. 1)[26]. Homopolymer PBTI (M_n 12.7 kDa) had μ_e of 1.53 cm^2/(V·s). By using off-center spin-coating, the μ_e further increased to 3.71 cm^2/(V·s).

Shi *et al.*[27] prepared distannylated bithiophene imide (BTI-Tin), and polymerized it with other electron-deficient units to give various A–A type polymers with high molecular weights. They optimized the synthetic routes to give PBTI with high M_n of 35.5 kDa, which showed a μ_e of 2.6 cm^2/(V·s) in OTFTs. They also studied the PBTI with different M_n as acceptor in PSCs. The device with PBTI (M_n 12.7 kDa) and PBTI (M_n 35.5 kDa) as acceptors and PTB7-Th as the donor gave PCEs of 0.14% and 6.67%, respectively. BTI-based A–A type polymer L14[28] presented good device performance with a PCE of 14.3%. Polymerizing BTI-Tin with dibrominated naphthalene diimide (NDI-Br) and perylene diimide (PDI-Br) produced two A–A copolymers P(BTI-NDI) and P(BTI-PDI)[29]. When applying them as ETLs in planar p–i–n PVSCs, the devices gave PCEs of 19.5% and 20.8%, respectively, with negligible hysteresis. To solve the high LUMO issue caused by electron-rich thiophene moiety in BTI, Guo *et al.* synthesized a novel acceptor building block CNI[30] by incorporating strong electron-withdrawing cyano onto BTI. A–A type copolymer PCNI-BTI with low LUMO level was obtained, offering a σ of 23.3 S/cm and a PF of 10 mW/(m·K^2) in OTE. Huang *et al.* prepared A–A type copolymers based on isoindigo (IIG) and PDI, and used them as acceptors, yielding a PCE of 2.68%[31]. Liu *et al.* designed a series of A–A copolymers based on B←N embedded building blocks, and the all-PSCs with P-BN-IID as the acceptor achieved a PCE of 5.04%[32]. Recently, they also synthesized A–A type copolymers PBN-18 and PBN-19[33] with a strong electron-deficient BNBP unit. After n-doping, PBN-19 exhibited σ of 7.8 S/cm and PF of 24.8 μW/(m·K^2).

The A–A type polymers show great potential in OTFTs, PSCs, PVSCs and OTEs. The acceptor units are fewer than donor units, so more efforts should be devoted to developing novel electron-deficient building blocks.

Correspondence to: Y Q Shi, shiyq@ahnu.edu.cn; L M Ding, ding@nanoctr.cn

Received 8 JUNE 2021.

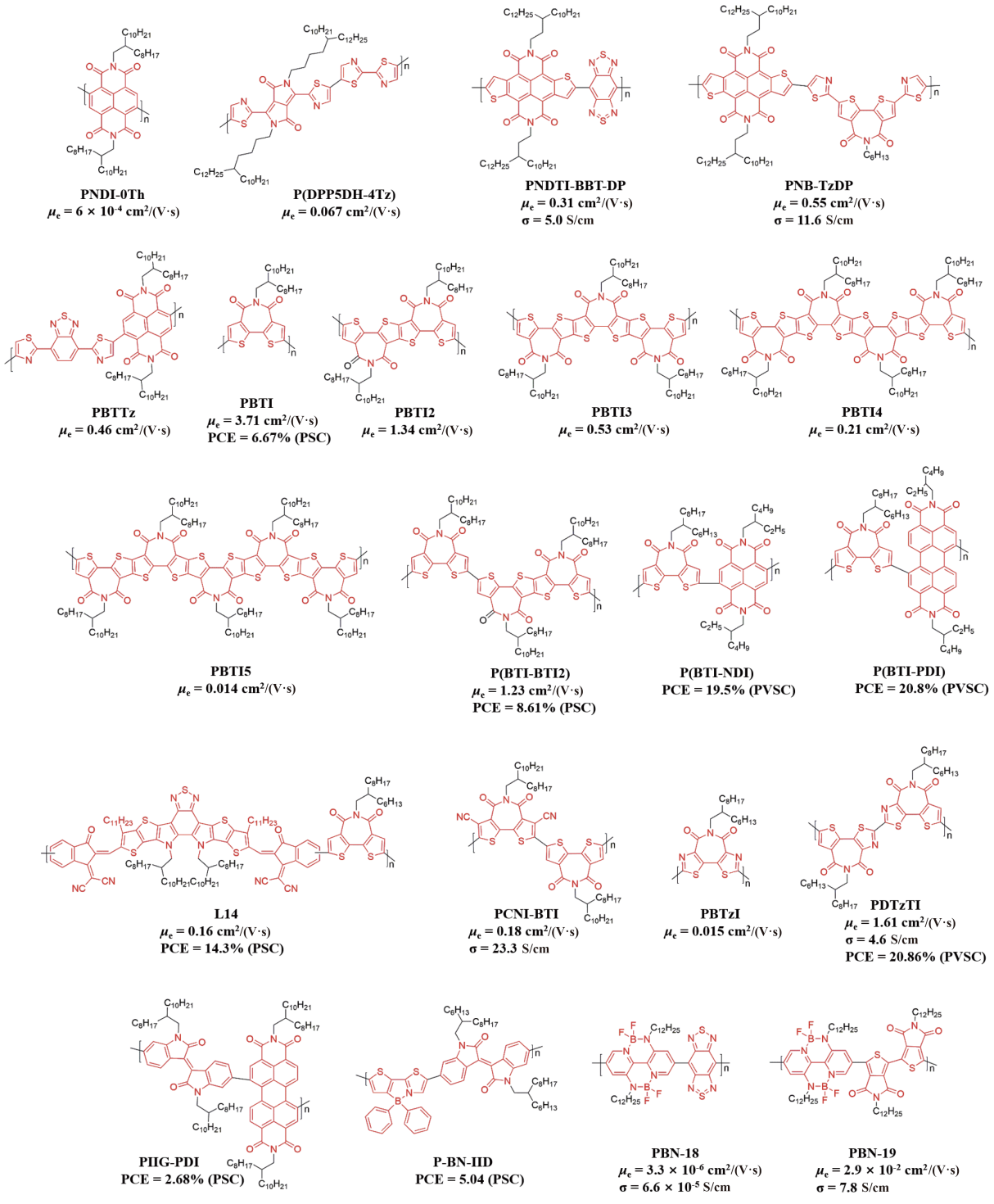

Fig. 1. Chemical structures of the representative n-type polymers with acceptor–acceptor backbone.

Acknowledgements

Y. Shi thanks the financial support from the Doctoral Research Initiation Foundation of Anhui Normal University (752091). L. Ding appreciates the National Key Research and Development Program of China (2017YFA0206600) and the National Natural Science Foundation of China (51773045, 21772030, 51922032, 21961160720) for financial support.

References

[1] Guo X, Facchetti A, Marks T J. Imide-and amide-functionalized polymer semiconductors. Chem Rev, 2014, 114, 8943

[2] Liu Q, Jiang Y, Jin K, et al. 18% efficiency organic solar cells. Sci Bull, 2020, 65, 272

[3] Jin K, Xiao Z, Ding L. D18, an eximious solar polymer!. J Semicond, 2021, 42, 010502

[4] Tang A, Xiao Z, Ding L, et al. ~1.2 V open-circuit voltage from organic solar cells. J Semicond, 2021, 42, 070202

[5] Jin K, Xiao Z, Ding L. 18.69% PCE from organic solar cells. J Semicond, 2021, 42, 060502

[6] Ji X, Xiao Z, Sun H, et al. Polymer acceptors for all-polymer solar cells. J Semicond, 2021, 42, 080202

[7] Jin K, Hao F, Ding L. Solution-processable n-type organic thermoelectric materials. Sci Bull, 2020, 65, 1862

[8] Zhang F, Di C. Exploring thermoelectric materials from high mobility organic semiconductors. Chem Mater, 2020, 32, 2688
[9] Lu Y, Wang J, Pei J. Strategies to enhance the conductivity of n-type polymer thermoelectric materials. Chem Mater, 2019, 31, 6412
[10] Yan X, Xiong M, Li J, et al. Pyrazine-Flanked diketopyrrolopyrrole (DPP): A new polymer building block for high-performance n-type organic thermoelectrics. J Am Chem Soc, 2019, 141, 20215
[11] Liu J, Ye G, Zee B, et al. N-type organic thermoelectrics of donor–acceptor copolymers: Improved power factor by molecular tailoring of the density of states. Adv Mater, 2018, 30, 1804290
[12] Ke L, Ding L. Perovskite crystallization. J Semicond, 2021, 42, 080203
[13] Li B, Yang K, Liao Q, et al. Imide-functionalized triarylamine-based donor-acceptor polymers as hole transporting layers for high-performance inverted perovskite solar cells. Adv Funct Mater, 2021, 2100332
[14] Wang Y, Chen W, Wang L, et al. Dopant-free small-molecule hole-transporting material for inverted perovskite solar cells with efficiency exceeding 21%. Adv Mater, 2019, 31, 1902781
[15] Yang J, Zhao Z, Wang S, et al. Insight into high-performance conjugated polymers for organic field-effect transistors. Chem, 2018, 4, 2748
[16] Durban M M, Kazarinoff P D, Luscombe C K. Synthesis and characterization of thiophene-containing naphthalene diimide n-type copolymers for OFET applications. Macromolecules, 2010, 43, 6348
[17] Wang Y, Nakano M, Michinobu T, et al. Naphthodithiophenediimide–benzobisthiadiazole-based polymers: Versatile n-type materials for field-effect transistors and thermoelectric devices. Macromolecules, 2017, 50, 857
[18] Wang Y, Takimiya K. Naphthodithiophenediimide–bithiopheneimide copolymers for high-performance n-type organic thermoelectrics: Significant impact of backbone orientation on conductivity and thermoelectric performance. Adv Mater, 2020, 32, 2002060
[19] Wang Y, Hasegawa T, Matsumoto H, et al. Significant difference in semiconducting properties of isomeric all-acceptor polymers synthesized via direct arylation polycondensation. Angew Chem Int Ed, 2019, 58, 11893
[20] Yuan Z, Fu B, Thomas S, et al. Unipolar electron transport polymers: A thiazole based all-electron acceptor approach. Chem Mater, 2016, 28, 6045
[21] Wang Y, Guo H, Ling S, et al. Ladder-type heteroarenes: Up to 15 rings with five imide groups. Angew Chem Int Ed, 2017, 56, 9924
[22] Shi Y, Guo H, Qin M, et al. Imide-functionalized thiazole-based polymer semiconductors: Synthesis, structure–property correlations, charge carrier polarity, and thin-film transistor performance. Chem Mater, 2018, 30, 7988
[23] Shi Y, Guo H, Qin M, et al. Thiazole imide-based all-acceptor homopolymer: Achieving high-performance unipolar electron transport in organic thin-film transistors. Adv Mater, 2018, 30, 1705745
[24] Liu J, Shi Y, Dong J, et al. Overcoming coulomb interaction improves free-charge generation and thermoelectric properties for n-doped conjugated polymers. ACS Energy Lett, 2019, 4, 1556
[25] Chen W, Shi Y, Wang Y, et al. N-type conjugated polymer as efficient electron transport layer for planar inverted perovskite solar cells with power conversion efficiency of 20.86%. Nano Energy, 2020, 68, 104363
[26] Wang Y, Guo H, Harbuzaru A, et al. (Semi)ladder-type bithiophene imide-based all-acceptor semiconductors: Synthesis, structure–property correlations, and unipolar n-type transistor performance. J Am Chem Soc, 2018, 140, 6095
[27] Shi Y, Guo H, Huang J, et al. Distannylated bithiophene imide: Enabling High-performance n-type polymer semiconductors with an acceptor–acceptor backbone. Angew Chem Int Ed, 2020, 59, 14449
[28] Sun H, Yu H, Shi Y, et al. A narrow-bandgap n-type polymer with an acceptor–acceptor backbone enabling efficient all-polymer solar cells. Adv Mater, 2020, 32, 2004183
[29] Shi Y, Chen W, Wu Z, et al. Imide-functionalized acceptor–acceptor copolymers as efficient electron transport layers for high-performance perovskite solar cells. J Mater Chem A, 2020, 8, 13754
[30] Feng K, Guo H, Wang J, et al. Cyano-functionalized bithiophene imide-based n-type polymer semiconductors: synthesis, structure–property correlations, and thermoelectric performance. J Am Chem Soc, 2021, 143, 1539
[31] Wang X, Lv L, Li L, et al. High-performance all-polymer photoresponse devices based on acceptor–acceptor conjugated polymers. Adv Funct Mater, 2016, 26, 6306
[32] Zhao R, Dou C, Xie Z, et al. Polymer acceptor based on B←N units with enhanced electron mobility for efficient all-polymer solar cells. Angew Chem Int Ed, 2016, 55, 5313
[33] Dong C, Deng S, Meng B, et al. Distannylated monomer of strong electron-accepting organoboron building block: Enabling acceptor–acceptor type conjugated polymers for n-type thermoelectric applications. Angew Chem Int Ed, 2021, in press

Yongqiang Shi received his PhD degree from Southwest Petroleum University in 2020. He was a visiting student in Xugang Guo Group at Southern University of Science and Technology in 2017-2020. In December 2020, he joined Anhui Normal University. His research focuses on the design and synthesis of n-type polymers for organic thin-film transistors, polymer solar cells, perovskite solar cells, and organic thermoelectrics.

Liming Ding got his PhD from University of Science and Technology of China (was a joint student at Changchun Institute of Applied Chemistry, CAS). He started his research on OSCs and PLEDs in Olle Inganäs Lab in 1998. Later on, he worked at National Center for Polymer Research, Wright-Patterson Air Force Base and Argonne National Lab (USA). He joined Konarka as a Senior Scientist in 2008. In 2010, he joined National Center for Nanoscience and Technology as a full professor. His research focuses on innovative materials and devices. He is RSC Fellow, the nominator for Xplorer Prize, and the Associate Editors for Science Bulletin and Journal of Semiconductors.