Conjugated Polymers Based on 1,8-Naphthalene Monoimide with High Electron Mobility

Guomin Zhu,[1†] Youdi Zhang,[1,2†] Yu Hu,[1] Xiaohong Zhao,[1] Zhongyi Yuan ,[1,2] Yiwang Chen [1,2]

[1]College of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China
[2]Jiangxi Provincial Key Laboratory of New Energy Chemistry/Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China
Correspondence to: Z. Yuan (E-mail: yuan@ncu.edu.cn)

Received 4 September 2017; accepted 3 October 2017; published online 00 Month 2017
DOI: 10.1002/pola.28891

ABSTRACT: 1,4,8,9-Naphthalene diimides (NDIs) with strong electron accepting ability and high stability are excellent building blocks for semiconductor polymers. However, 1,8-naphthalene monoimide (NMI) with similar structure and energy levels as that of NDI has never been used to construct conjugated polymers because of synthetic difficulty. Herein, 3,6-dibromo-NMI (DBNMI) with bulky alkyl groups was obtained effectively in a four-step synthesis, and three donor-acceptor (D-A) type conjugated polymers based on NMI were firstly prepared. These polymers have strong absorption in the range of 300–600 nm, low LUMO level of 3.68 eV, and moderate bandgaps of 2.18 eV. Space charge limiting current measurements indicate these polymers are typical electron transporting materials, and the highest electron mobility is up to 5.8×10^{-3} $cm^2 V^{-1} s^{-1}$, which is close to the star acceptor based on NDI (N2200, 5.0×10^{-3} $cm^2 V^{-1} s^{-1}$). © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

KEYWORDS: conjugated polymers; electron acceptor; naphthalene monoimide

INTRODUCTION Organic semiconductors are the focus of research in the past decades, because of their various applications in organic light emitting displays, printable electronic circuits, and organic solar cells.[1–3] Polymeric semiconductors (conjugated polymers) have drawn special attention compared to small molecule semiconductors, because they have advantages of good film forming properties, low cost solution process, and high carrier mobility.[4] Acceptors (n-type semiconductors, electron transporting materials) are much rarer compared with their donor counterparts (p-type semiconductors, hole transporting materials), and both of them are essential in electronic circuits. As for as star acceptors PCBM,[5–7] they have disadvantages of high cost, difficulties of modification, and weak absorption in a visible region.[8–10] Therefore, it is urgent to develop highly efficient polymeric acceptors.[11–15]

1,4,8,9-Naphthalene diimides (NDIs) with rigid conjugated cores, high stability, and strong electron accepting ability are excellent acceptors.[16–20] Polymeric acceptors with NDIs as acceptor parts have shown high performance in organic thin-film transistors (OTFTs) and organic solar cells.[21–25] Imide groups have been widely used to construct highly efficient acceptors, such as NDI,[26–28] phthalimide,[29–34] and perylene diimides derivatives.[35–39] 1,8-Naphthalene monoimide (NMI) with the similar structure and energy level as that of NDI, has been used to construct small functional molecules which were used in fluorescent probes, OTFTs and organic solar cells.[40–44] However, conjugated polymers based on NMI have never been reported due to the synthetic difficulty (Fig. 1).

In 2013, 3,6-dibromo-N-(2,4-diisopropylphenyl)-1,8-naphthalimide (DBDIPPNMI) was firstly synthesized by Hiroyuki et al. with the synthetic route shown in Figure 2.[45]. However, above brominated NMI with 2,4-diisopropylphenyl groups has poor solubility, and it is impossible to be used in conjugated polymers. To increase its solubility, we attempted to obtain DBNMI with bulky alkyl groups in literature method.[46–49] However, target compound was failed to obtain because of very difficult purification of crude products, which stimulates us to develop a new synthetic route for efficient synthesis of soluble DBNMI for conjugated polymers.

[†]Guomin Zhu and Youdi Zhang contributed equally to this work

Additional Supporting Information may be found in the online version of this article.

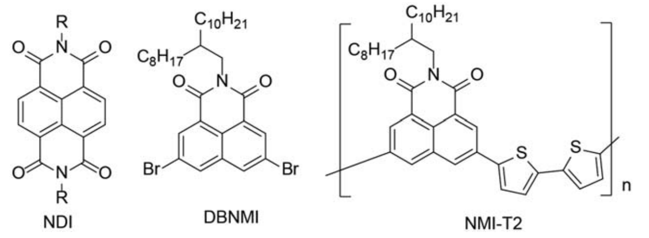

FIGURE 1 Structures of NDI, DBNMI, and NMI-T2.

Herein, a new synthetic route was presented. As shown in Figure 3, soluble DBNMI was efficiently synthesized with a four-step route. Three D-A type conjugated polymers based on NMI were firstly prepared by coupling reactions of DBNMI with excellent donors 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (T2), 5,5″-bis(trimethylstannyl)-2,2′:5′,2″-terthiophene (T3), and (4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT). These polymers are proved to be typical acceptors, and the highest mobility is as high as 5.8×10^{-3} $cm^2\ V^{-1}\ s^{-1}$, which is close to star molecule Poly{[*N,N'*-bis(2-octy ldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2-bithio-phene)10 (N2200, Figure S1, Supporting Information).

EXPERIMENTAL

Materials and Methods

All the chemicals in this research are commercially available. The ^1H and ^{13}C NMR spectra were measured on a NMR spectrometer with $CDCl_3$ as a solvent and TMS as an internal reference. Cyclic voltammetry (CV) of acceptors in the thin film was performed with a standard commercial electrochemical analyzer in a three electrode single component cell under argon. Working electrode: glassy carbon; reference electrode: Ag/Ag^+, auxiliary electrode: Pt wire; supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scan rate of 100 mV s^{-1}, internal standard: ferrocene (Fc). UV–vis absorption spectra were taken on a Hitachi U-3100 UV–vis spectrophotometer. Thermogravimetric analysis (TGA) measurement was performed on a TA Instruments, TGA-2050. By the GPC method, and polystyrene was used as a standard by using 1,2,4-trichlorobenzene as eluent under 160 °C.

Synthesis of DNNMA

1,8-Naphthalic anhydride (NMA; 10 g, 50.5 mmol) was dissolved in 35 mL 98% H_2SO_4 at 0 °C, and the mixture of 98% H_2SO_4 (20 mL) and 68% HNO_3 (15 mL) was dropwisely added to above NMA solution. The reaction was kept at 0 °C for 1 h, and at 65 °C for extra 1.5 h. The mixture was poured into the ice, filtered, washed with water and ethanol. The filter cake was collected and recrystallized from acetic acid. The crude DNNMA was obtained as a white solid. It was used directly in the next step without further purification.

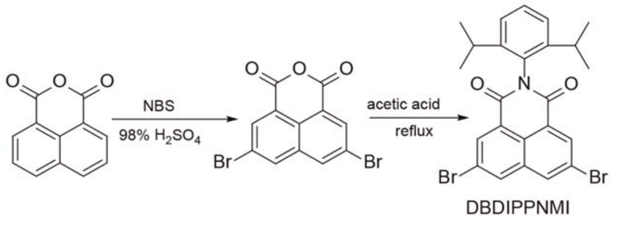

FIGURE 2 Synthetic route for DBDIPPNMI in literature.

Synthesis of DNNMI

A mixture of DNNMA (5 g, 17.4 mmol), 2-octyl-dodecylamine (7.6 g, 25.6 mmol), and 100 mL CH_3COOH was refluxed for 3 h. The mixture was extracted with CH_2Cl_2, and purified through the silica gel column. The eluent is petroleum ether/CH_2Cl_2 (1:1, v/v). DNNMI (6.12 g, 62%) was obtained as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 2H), 9.33 (s, 2H), 4.16 (d, 2H), 1.97 (s, 1H), 1.23 (s, 32H), 0.86 (q, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 147.7, 132.0, 130.7, 130.2, 127.3, 125.3, 77.3, 77.0, 76.7, 45.3, 36.6, 319, 31.6, 30.0, 29.8, 29.3, 26.4, 22.7, 14.1 ppm. MP: 78 °C. MS (MALDI-TOF): Calcd for $C_{32}H_{45}N_3O_6$: 567.33, found: 567.70 (M-).

Synthesis of DANMI

A mixture of DNNMI (5.0 g, 8.8 mmol), 5% Pd/C (0.6 g), and 20 mL THF was added to the autoclave, and it was filled with H_2, heated at 80 °C for 6 h. Filtrate was collected by filtration, solvent was removed, and the crude product was purified through the silica gel column with eluent CH_2Cl_2. DANMI (3.5 g, 78%) was obtained as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H), 7.05 (d, 2H), 4.05 (d, 6H), 1.96 (d, 1H), 1.25 (d, 32H), 0.86 (q, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 145.5, 135.2, 123.5, 118.5, 117.4, 111.9, 77.3, 77.0, 76.7, 44.4, 36.6, 31.9, 31.6, 30.1, 29.6, 29.3, 26.5, 22.7, 14.1 ppm. MP: 132 °C.HRMS (MALDI-TOF): Calcd for $C_{32}H_{49}N_3O_2$: 507.3825, found: 507.3816 (M–).

Synthesis of DBNMI

DANMI (2.0 g, 3.9 mmol) and 40% aqueous HBr solution (200 mL) were mixed at −5 °C; 0.4 mol/L $NaNO_2$ aqueous solution (120 mL) was dropwisely added to above mixture. Then, the mixture of CuBr (3.0 g, 20.9 mmol) and 40% aqueous HBr solution (120 mL) was added at −5 °C for 3 h. The mixture was extracted with CH_2Cl_2, and purified through the silica gel column. The eluent is petroleum ether/CH_2Cl_2 (2:1, v/v). DBNMI (0.7g, 27%) was obtained as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 2H), 8.27 (s, 2H), 4.08 (d, 2H), 1.98 (d, 1H), 1.24 (d, 32H), 0.99 – 0.69 (q, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 134.1, 124.4, 122.3, 77.3, 76.9, 76.6, 44.9, 36.5, 31.8, 29.9, 29.6, 29.4, 26.4, 22.6, 14.0 ppm. MP: 92 °C. MS (MALDI-TOF): Calcd for $C_{32}H_{45}Br_2NO_2$: 633.18, found: 633.23 (M–).

Synthesis of NMI-T2

A mixture of DBNMI (299.3 mg, 0.5 mmol), T2 (232.2 mg, 0.5 mmol), $Pd(PPh_3)_4$ (32.6 mg, 0.03 mmol), toluene (10 mL), and DMF (1 mL) was refluxed for 24 h under argon. The crude product precipitated in methanol and was collected by filtration. This solid purified through the silica

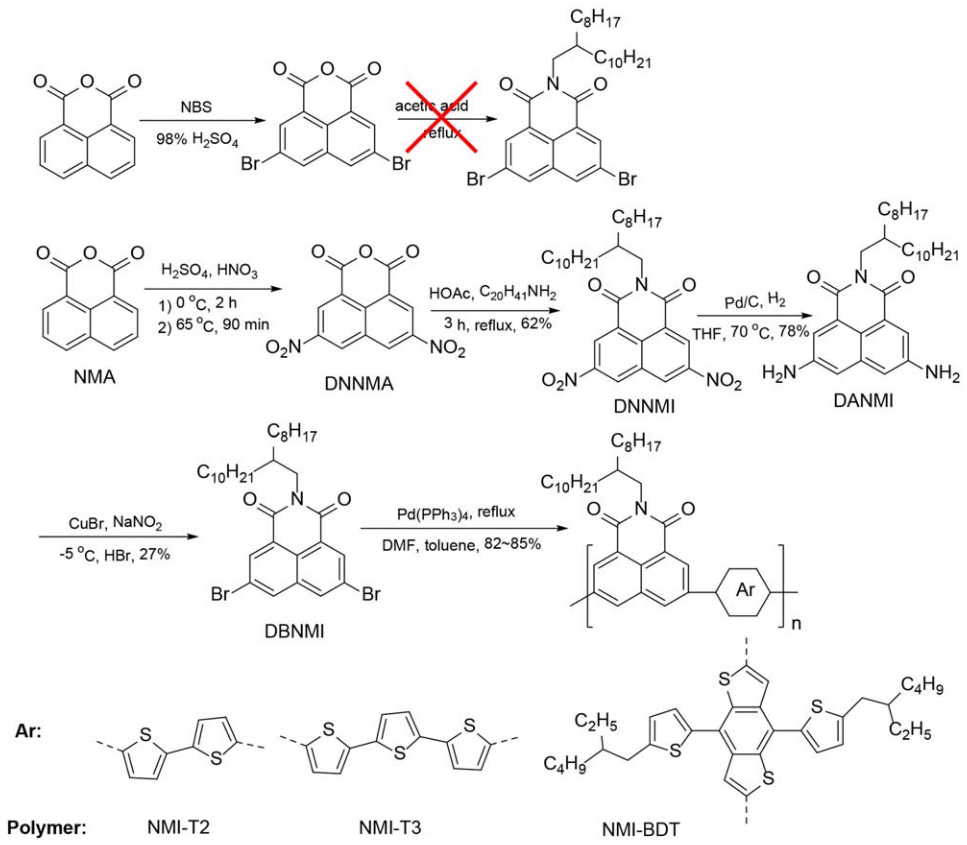

FIGURE 3 Synthetic route of DBNMI and related polymers. [Color figure can be viewed at wileyonlinelibrary.com]

gel column, and the eluent is $CHCl_3$. NMI-T2 (446.5 mg, 84% yield) was obtained as a dark red solid. $M_n = 5.9$ KDa, $M_w/M_n = 1.32$; UV–vis ($CHCl_3$): λ_{max} (ε) = 370 nm (23,100 M^{-1} cm^{-1}).

Synthesis of NMI-T3

A mixture of DBNMI (298.7 mg, 0.5 mmol), T3 (270.9 mg, 0.5 mmol), $Pd(PPh_3)_4$ (32.6 mg, 0.03 mmol), toluene (10 mL), and DMF (1 mL) was refluxed for 24 h under argon. The crude product precipitated in methanol and was collected by filtration. This solid purified through the silica gel column, and the eluent is $CHCl_3$. NMI-T3 (484.2 mg, 85% yield) was obtained as a dark red solid. $M_n = 4.8$ KDa, $M_w/M_n = 1.62$; UV–vis ($CHCl_3$): λ_{max} (ε) = 414 nm (38,900 M^{-1} cm^{-1}).

TABLE 1 Molecular Weights of the Polymers[a]

Polymer	M_n (KDa)	M_w (KDa)	M_w/M_n
NMI-T2	5.9	7.8	1.32
NMI-T3	4.8	7.8	1.62
NMI-BDT	52.1	99.3	1.91

[a] 1,2,4-Trichlorobenzene as eluent, under 160 °C, and polystyrene as standard.

Synthesis of NMI-BDT

A mixture of DBNMI (191.4 mg, 0.3 mmol), BDT (271.0 mg, 0.3 mmol), $Pd(PPh_3)_4$ (20.8 mg, 0.02 mmol), toluene (10 mL), and DMF (1 mL) was refluxed for 24 h under argon. The crude product precipitated in methanol and was collected by filtration. This solid purified through the silica gel column, and the eluent is $CHCl_3$. NMI-BDT (379.2 mg, 82% yield) was obtained as a dark red solid. $M_n = 52.1$ KDa,

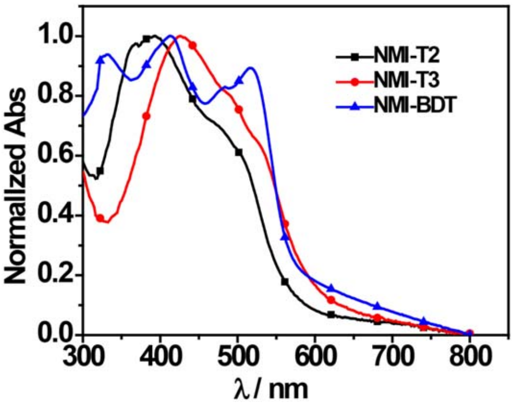

FIGURE 4 Absorption spectra of NMI-T2, NMI-T3, and NMI-BDT in solid film. [Color figure can be viewed at wileyonlinelibrary.com]

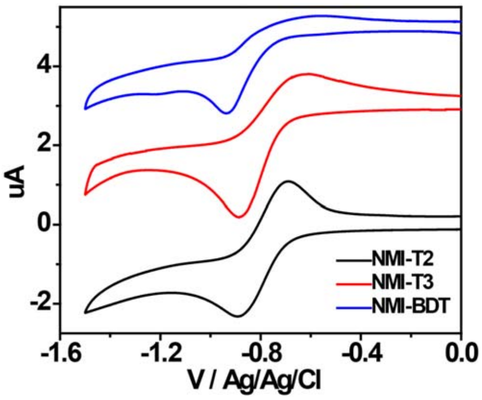

FIGURE 5 Cyclic voltammograms of NMI-T2, NMI-T3, and NMI-BDT. [Color figure can be viewed at wileyonlinelibrary.com]

$M_w/M_n = 1.91$; UV–vis ($CHCl_3$): λ_{max} (ε) = 410 nm (49,300 M^{-1} cm^{-1}).

RESULTS AND DISCUSSION

Synthesis

As shown in Figure 2, we failed to get pure DBNMI in literature method, because the crude product contains a main side product, which has a very similar retention factor value in TLC as that of DBNMI. Therefore, we adopted a new synthetic route. The key intermediate DBNMI was obtained through a four-step synthesis.

3,6-Dinitro-1,8-naphthalic anhydride (DNNMA) was obtained by nitration of commercial NMA at 70 °C in the mixture of 98% H_2SO_4 and 68% HNO_3.The low reaction temperature is necessary, which could improve the yield of DNNMA.

DNNMA and 2-octyldodecylamine was refluxed in acetic acid to give 3,6-dinitro-N-(2-octyldodecyl)-1,8-naphthalene imide (DNNMI) in 62% yield.[50] Since the nitro group can be substituted by amino groups, we tried different solvents, such as ethanol and *N*,*N*-dimethylformamide, and found that acetic acid is the best solvent.

3,6-Diamino-*N*-(2-octyldodecyl)-1,8-naphthalimide (DANMI) was obtained by hydrogenation of DNNMI in THF with catalyst 5% Pd/C, and the isolated yield is up to 77%.[51] The product can be separated by neutral alumina column, or separated by a silica column treated with trimethylamine.

The key intermediate 3,6-dibromo-*N*-(2-octyldodecyl)-1,8-naphthalimide (DBNMI) was obtained by bromination of DANMI. The product can be rapidly separated by a silica gel column.

With DBNMI as acceptor part, three D-A type conjugated polymers were obtained by Stille coupling reactions. The coupling reactions occur smoothly in refluxed toluene at the presence of catalyst $Pd(PPh_3)_4$, and the yield is over 80%. To improve the activity of the catalyst, a small amount of DMF was added.

The structures of new compounds DNNMI, DANMI, and DBNMI were well characterized by ^1H NMR, ^{13}C NMR, and MS. The polymers NMI-T2, NMI-T3, and NMI-BDT were characterized by gel permeation chromatography (GPC).

Number-average molecular weight (M_n) of NMI-T2, NMI-T3, and NMI-BDT are 5.9, 4.8, 52.1 KDa respectively, which was measured by GPC using 1,2,4-trichlorobenzene as eluent under 160 °C and polystyrene as the standard. The molecular weight of NMI-T2 and NMI-T3 is low because of their poor solubility. High molecular weight of NMI-BDT was obtained, because the donor monomer BDT contains soluble alkyl chains. All three polymers are soluble in chloroform, chlorobenzene and other organic solvents, which guarantees their solution process (Table 1).

Optical Properties

The UV–vis absorption spectra of NMI-T2, NMI-T3, and NMI-BDT in thin film are illustrated in Figure 4. These polymers have strong absorption in the range of 350–550 nm. Compared to the NDI polymers, maximum absorption of polymer NMI-T2 show significant blue shift by 286 nm, and other polymers also have similar blue shifts,[52] because of less electron withdrawing imide groups. In solution (Figure S2, Supporting Information), the maximum extinction coefficients (ε_{max}) of NMI-T2, NMI-T3, and NMI-BDT are around 23,000–50,000 M^{-1} cm^{-1} located at 370, 414, and 410 nm, respectively. Compared with solution absorption, solid absorption redshifts more than 50 nm, indicating strong aggregation of NMI polymers in solid state. The optical band gaps of NMI-T2, NMI-T3, and NMI-BDT were estimated from the absorption onset edge of the thin films, and the values are of 2.18, 2.06, and 2.16 eV, respectively. Therefore, these polymers are moderate bandgaps acceptors. Medium

TABLE 2 Optical and Electrochemical Data of NMI-T2, NMI-T3, and NMI-BDT

Polymers	λ^{abs} (nm)		$\varepsilon_{max}{}^a$ ($M^{-1}cm^{-1}$)	$\lambda_{on\ set}{}^b$ (nm)	$E_g{}^c$ (eV)	LUMO (eV)	HOMO (eV)
	Solution	Film					
NMI-T2	370	392	23,100	569	2.18	−3.68	−5.86
NMI-T3	414	428	38,900	602	2.06	−3.67	−5.73
NMI-BDT	329/410/515	330/414/519	49,300	574	2.16	−3.66	−5.82

[a] The molar extinction coefficient at λ_{max} in solution.
[b] Measured in thin films.
[c] Optical band gap.

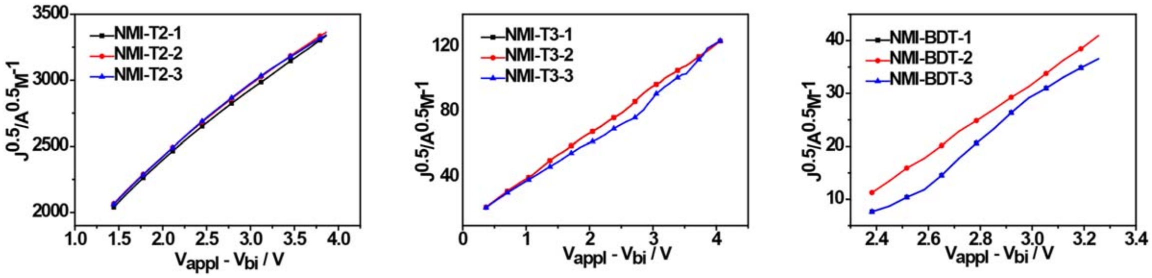

FIGURE 6 Plots for the measurements of electron mobility of NMI-T2, NMI-T3, and NMI-BDT. [Color figure can be viewed at wileyonlinelibrary.com]

bandgap acceptors with excellent photovoltaic properties are highly desired in the organic solar cells.[53,54]

Electrochemical Properties

To study the energy levels of these polymers, their redox properties in the solid state were measured by the CV. All of them show a semi-reversible reduction peak indicating their ability to accepting at least one electron (Fig. 5). The LUMO levels were estimated based on the assumption that the energy level of Fc/Fc^+ is -4.8 eV relative to vacuum,[55] and all three polymers show similar LUMO energy levels in $-3.66\sim-3.68$ eV. The reason is that all the polymers have the same first electron accepting position (O atom in the carbonyl group), and the carbonyl groups in these polymers have little energy difference. The HOMO energy levels were calculated by equation of HOMO = LUMO – E_g, and the values are -5.86, -5.73, and -5.82 eV for NMI-T2, NMI-T3, and NMI-BDT, respectively. Compared with the NDI polymers, LUMO levels of NMI polymers increased by about 0.25 eV, which lies in less electron withdrawing imide groups of NMI polymers (Table 2).

Charge Mobility

Space charge limiting current (SCLC) is a widely used method to estimate the electron transport properties of semiconductors. In this research, the electron mobility was measured by SCLC devices with the structure of ITO/ZnO/polymer film/Al. The current-voltage curves were shown in Figure 6. The electron mobility of NMI-T2, NMI-T3, and NMI-BDT is 4.9 (±0.9) $\times10^{-3}$, 1.0 (±0.3) $\times10^{-5}$, 3.1 (±0.3) $\times10^{-3}$ $cm^2\ V^{-1}\ s^{-1}$ respectively. The highest electron mobility is up to 5.8×10^{-3} $cm^2{\cdot}V^{-1}\ s^{-1}$, which is close to star N2200 (5×10^{-3} $cm^2\ V^{-1}\ s^{-1}$, SCLC method).[56]

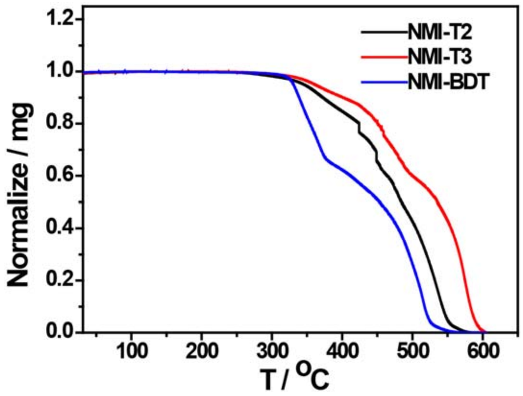

FIGURE 7 TGA plots of NMI-T2, NMI-T3, and NMI-BDT (heating rate: 10 °C min^{-1}, under air atmosphere). [Color figure can be viewed at wileyonlinelibrary.com]

Thermal Stability

As shown in Figure 7, all three polymers exhibit good thermal stability in TGA, and 5% weight loss temperature is higher than 330 °C under the air. Different scanning calorimetry traces (Figure S3, Supporting Information) of NMI-T2, NMI-T3 and NMI-BDT show no phase transition from room temperature to 250 °C.

CONCLUSIONS

In conclusion, soluble DBNMI was obtained efficiently through a new synthetic route. Three D-A types conjugated polymers based on NMI was first prepared. These polymers have low LUMO levels, moderate bandgaps, and strong absorption. They show typical characters of n-type semiconductors in SCLC measurements, and the highest electron mobility is up to 5.8×10^{-3} $cm^2\ V^{-1}\ s^{-1}$. These polymers are a class of excellent electron transport materials and are expected to be widely used in the organic optoelectronics. Their applications in OTFTs and organic solar cells are in progress in our laboratory.

ACKNOWLEDGMENTS

The work was supported by grants National Natural Science Foundation of China (No. 21562031 and 21602150), and Natural Science Foundation of Jiangxi Province in China (No. 20161BAB213064, 20171ACB21012, 20161BAB213063, and 20142BAB213005). The authors declare no competing financial interest.

REFERENCES AND NOTES

1 C. W. Tang, *Appl Phys Lett.* **1986**, *48*, 183.

2 L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus, R. H. Friend, *Nature.* **2005**, *434*, 194.

3 Q. Tai, F. Yan, *Adv. Mater.* **2017**, *29*, 1700192.

4 V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Brédas, *Chem. Rev.* **2007**, *107*, 926.

5 V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya, H. Murata, *Nat. Photon.* **2015**, *9*, 403.

6 Z. Wu, C. Sun, S. Dong, X.-F. Jiang, S. Wu, H. Wu, H.-L. Yip, F. Huang, Y. Cao, *J. Am. Chem. Soc.* **2016**, *138*, 2004.

7 J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, *Nat. Commun.* **2013**, *4*, 1446.

8 I. Etxebarria, J. Ajuria, R. Pacios, *J Photon Energy.* **2015**, *5*, 057214.

9 A. Heeger, *J. Adv. Mater.* **2014**, *26*, 10.

10 M. C. Scharber, *Adv. Mater.* **2016**, *28*, 1994.

11 Y. Lin, J. Wang, Z. G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan, *Adv. Mater.* **2015**, *27*, 1170.

12 F. Zhao, S. Dai, Y. Wu, Q. Zhang, J. Wang, L. Jiang, Q. Ling, Z. Wei, W. Ma, W. You, C. Wang, X. Zhan, *Adv. Mater.* **2017**, *29*, 1700144.

13 D. Meng, H. Fu, C. Xiao, X. Meng, T. Winands, W. Ma, W. Wei, B. Fan, L. Huo, N. L. Doltsinis, Y. Li, Y. Sun, Z. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 10184.

14 Q. Wu, D. Zhao, A. M. Schneider, W. Chen, L. Yu, *J. Am. Chem. Soc.* **2016**, *138*, 7248.

15 D. Meng, D. Sun, C. Zhong, T. Liu, B. Fan, L. Huo, Y. Li, W. Jiang, H. Choi, T. Kim, *J. Am. Chem. Soc.* **2015**, *138*, 375.

16 D. Mori, H. Benten, I. Okada, H. Ohkita, S. Ito, *Energy Environ. Sci.* **2014**, *7*, 2939.

17 L. Gao, Z. G. Zhang, L. Xue, J. Min, J. Zhang, Z. Wei, Y. Li, *Adv. Mater.* **2016**, *28*, 1884.

18 H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti, *Nature.* **2009**, *457*, 679.

19 F. Zhang, Y. Hu, T. Schuettfort, C.-A. Di, X. Gao, C. R. McNeill, L. Thomsen, S. C. B. Mannsfeld, W. Yuan, H. Sirringhaus, D. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 2338.

20 S. Ito, T. Hirata, D. Mori, H. Benten, L.-T. Lee, H. Ohkita, *J. Photopolym. Sci. Technol.* **2013**, *26*, 175.

21 M. M. Durban, P. D. Kazarinoff, Y. Segawa, C. K. Luscombe, *Macromolecules.* **2011**, *44*, 4721.

22 P. M. Alvey, R. J. Ono, C. W. Bielawski, B. L. Iverson, *Macromolecules.* **2013**, *46*, 718.

23 S. Shi, J. Yuan, G. Ding, M. Ford, K. Lu, G. Shi, J. Sun, X. Ling, Y. Li, W. Ma, *Adv. Funct. Mater.* **2016**, *26*, 5669.

24 Y. Kim, J. Hong, J. H. Oh, C. Yang, *Chem. Mater.* **2013**, *25*, 3251.

25 X. Guo, M. D. Watson, *Org. Lett.* **2008**, *10*, 5333.

26 J. Choi, K.-H. Kim, H. Yu, C. Lee, H. Kang, I. Song, Y. Kim, J. H. Oh, B. J. Kim, *Chem. Mater.* **2015**, *27*, 5230.

27 S. Subramaniyan, T. Earmme, N. M. Murari, S. A. Jenekhe, *Polym. Chem.* **2014**, *5*, 5707.

28 T. Sajoto, S. P. Tiwari, H. Li, C. Risko, S. Barlow, Q. Zhang, J.-Y. Cho, J.-L. Brédas, B. Kippelen, S. R. Marder, *Polymer.* **2012**, *53*, 1072.

29 M. Gsänger, J. H. Oh, M. Könemann, H. W. Höffken, A. M. Krause, Z. Bao, F. Würthner, *Angew. Chem.* **2010**, *122*, 752.

30 Z. Liu, G. Zhang, Z. Cai, X. Chen, H. Luo, Y. Li, J. Wang, D. Zhang, *Adv. Mater.* **2014**, *26*, 6965.

31 J. T. Bloking, X. Han, A. T. Higgs, J. P. Kastrop, L. Pandey, J. E. Norton, C. Risko, C. E. Chen, J.-L. Brédas, M. D. McGehee, A. Sellinger, *Chem. Mater.* **2011**, *23*, 5484.

32 H. Li, F. S. Kim, G. Ren, E. C. Hollenbeck, S. Subramaniyan, S. A. Jenekhe, *Angew. Chem. Int. Ed.* **2013**, *52*, 5513.

33 T. Okamoto, T. Suzuki, H. Tanaka, D. Hashizume, Y. Matsuo, *Chem.-Asian J.* **2012**, *7*, 105.

34 C.-C. Kao, P. Lin, C.-C. Lee, Y.-K. Wang, J.-C. Ho, Y.-Y. Shen, *Appl. Phys. Lett.* **2007**, *90*, 212101.

35 W. Chen, X. Yang, G. Long, X. Wan, Y. Chen, Q. Zhang, *J. Mater. Chem. C* **2015**, *3*, 4698.

36 Y. Liu, J. Y. L. Lai, S. Chen, Y. Li, K. Jiang, J. Zhao, Z. Li, H. Hu, T. Ma, H. Lin, *J. Mater. Chem. A* **2015**, *3*, 13632.

37 S. Long, Y. Wang, S. Vdović, M. Zhou, L. Yan, Y. Niu, Q. Guo, A. Xia, *Phys. Chem. Chem. Phys.* **2015**, *17*, 18567.

38 J. Zhao, Y. Li, J. Zhang, L. Zhang, J. Y. L. Lai, K. Jiang, C. Mu, Z. Li, C. L. C. Chan, A. Hunt, S. Mukherjee, H. Ade, X. Huang, H. Yan, *J. Mater. Chem. A* **2015**, *3*, 20108.

39 X. Zhang, J. Yao, C. Zhan, *Chem. Commun.* **2015**, *51*, 1058.

40 J. Zhang, X. Zhang, H. Xiao, G. Li, Y. Liu, C. Li, H. Huang, X. Chen, Z. Bo, *ACS Appl. Mater. Inter.* **2016**, *8*, 5475.

41 X. Zhang, J. Zhang, H. Lu, J. Wu, G. Li, C. Li, S. Li, Z. Bo, *J. Mater. Chem. C* **2015**, *3*, 6979.

42 J. Zhang, H. Xiao, X. Zhang, Y. Wu, G. Li, C. Li, X. Chen, W. Ma, Z. Bo, *J. Mater. Chem. C* **2016**, *4*, 5656.

43 L. Duan, Y. Xu, X. Qian, F. Wang, J. Liu, T. Cheng, *Tetrahedron Lett.* **2008**, *49*, 6624.

44 I. Grabtchev, T. Philipova, P. Meallier, S. Guittonneau, *Dyes Pigments.* **1996**, *31*, 31.

45 J. Y. Xue, W. Nakanishi, D. Tanimoto, D. Hara, Y. Nakamura, H. Isobe, *Tetrahedron Lett.* **2013**, *54*, 4963.

46 H. Fu, D. Meng, X. Meng, X. Sun, L. Huo, Y. Fan, Y. Li, W. Ma, Y. Sun, Z. Wang, *J. Mater. Chem. A* **2017**, *5*, 3475.

47 X. Lian, L. Zhang, Y. Hu, Y. Zhang, Z. Yuan, W. Zhou, X. Zhao, Y. Chen, *Org. Electron.* **2017**, *47*, 72.

48 Y. Zhou, T. Kurosawa, W. Ma, Y. Guo, L. Fang, K. Vandewal, Y. Diao, C. Wang, Q. Yan, J. Reinspach, J. Mei, A. L. Appleton, G. I. Koleilat, Y. Gao, S. C. B. Mannsfeld, A. Salleo, H. Ade, D. Zhao, Z. Bao, *Adv. Mater.* **2014**, *26*, 3767.

49 L. Fang, Y. Zhou, Y.-X. Yao, Y. Diao, W.-Y. Lee, A. L. Appleton, R. Allen, J. Reinspach, S. C. Mannsfeld, Z. Bao, *Chem. Mater.* **2013**, *25*, 4874.

50 R. W. Middleton, J. Parrick, *J. Heterocycl. Chem.* **1985**, *22*, 1567.

51 S. Girouard, M.-H. Houle, A. Grandbois, J. W. Keillor, S. W. Michnick, *J. Am. Chem. Soc.* **2005**, *127*, 559.

52 Z. Chen, Y. Zheng, H. Yan, A. Facchetti, *J. Am. Chem. Soc.* **2009**, *131*, 8.

53 S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.* **2011**, *133*, 4625.

54 Y. Dong, X. Hu, C. Duan, P. Liu, S. Liu, L. Lan, D. Chen, L. Ying, S. Su, X. Gong, F. Huang, Y. Cao, *Adv. Mater.* **2013**, *25*, 3683.

55 Y. Hu, S. Chen, L. Zhang, Y. Zhang, Z. Yuan, X.-H. Zhao, Y. Chen, *J. Org. Chem.* **2017**, *82*, 5926.

56 R. Steyrleuthner, M. Schubert, F. Jaiser, J. C. Blakesley, Z. Chen, A. Facchetti, D. Neher, *Adv. Mater.* **2010**, *22*, 2799.