Synthesis and Characterization of 2-Alkylbenzotriazole-Based Donor- π -Acceptor-Type Copolymers

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Abstract: Four donor- π -acceptor-type copolymers were synthesized via palladium-catalyzed Sonogashira coupling reaction. The resulting donor- π -acceptor-conjugated copolymers can show fluorescence emission in the range of $\lambda = 473-568$ nm, and the band gaps of the alternating polymers can be tuned in the range 3.09–3.74 eV by using four different donors.

Key words: donor- π -acceptor, conjugated copolymers, benzotriazoles, fluorescence

Conjugated polymers (CP) incorporating different electron-donating (D) units and electron-accepting (A) heterocycle groups have attracted much more attention on many optoelectronic applications of prospective materials.¹ In recent years, many ground-breaking contributions have been devoted to the construction of novel multifunctional polymer materials due to their advantages on low cost, mechanical flexibility, low weight, large-scale production, and so on.² One of the plausible strategies has been confirmed by designing D-A-type polymers at welldefined molecular level, which can tune the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels to absorb visible wavelength photons as well as enhance the intramolecular charge transfer (ICT) efficiency.³ Recently, many novel D-A polymers have been widely explored by introducing various strong electron-rich groups and electron-accepting counterparts in the main chain backbone.⁴ Compared with D-A-type polymers, the D- π -A counterparts can also exhibit excellent photovoltaic properties due to the effective charge transport along the delocalized π -conjugation polymer backbone.⁵ To the best of our knowledge, the work on the design and synthesis of D- π -A-type polymers still remains elusive.

2-Alkylbenzotriazole (BTA) has been wildly employed as an electron-accepting moiety in the past years.⁶ However, incorporation of BTA into D- π -A-conjugated polymer main chain received less attention.⁷ Chen reported three BTA-based conjugated polymers with good solubility in common organic solvents and good thermal stability.⁸ The You group also designed D- π -A-type copolymers based on the BTA group which show high hole mobility and high power conversion efficiency (PCE) up to 7%.⁹ In this

SYNLETT 2013, 24, 1505–1508 Advanced online publication: 14.06.2013 DOI: 10.1055/s-0033-1339177; Art ID: ST-2013-W0300-L © Georg Thieme Verlag Stuttgart · New York paper we synthesized four novel D- π -A-conjugated copolymers by using alkyl-substituted phenothiazine and thiophene as donors, 2-alkylbenzotriazole as acceptor, and alkyne linker as π -bridge linker.

The monomers and four polymers were synthesized as shown in Scheme 1. Compound 2,¹⁰ 3,7-dibromo-10-octadecyl-10*H*-phenothiazine (M2),¹¹ 3,7-dibromo-10-octadecyl-10*H*-phenothiazine-5,5-dioxide (M3),¹² and 3,7bis(5-bromothiophen-2-yl)-10-octadecyl-10H-phenothiazine (M4),¹³ and 3,7-bis(5-bromothiophen-2-yl)-10octadecyl-10*H*-phenothiazine-5,5-dioxide $(M5)^{12}$ were prepared according to the literature. 4,7-Diethynyl-2octyl-2*H*-benzo[d][1,2,3]triazole (M1) could be obtained by Sonogashira coupling reaction of 4,7-dibromo-2-octyl-2H-benzo[d][1,2,3]triazole (2) with trimethylsilylacetylene (TMSA), and then the hydrolytic reaction was carried out by a KOH solution. D- π -A-type copolymers of P1, P2, P3, and P4 were synthesized via Sonogashira cross-coupling reaction of M1 with M2, M3, M4, and M5 by using $Pd(PPh_3)_4$ as a catalyst in DMF-Et₃N at 80 °C for 48 hours under N₂ atmosphere, respectively.¹⁴ These resulting D-π-A-conjugated copolymers show fluorescence emission in the range of $\lambda = 473-568$ nm, and the band gaps of the copolymers can be tuned in the range of 3.09–3.74 eV, which is attributed to the minimization of steric effects between donator and acceptor. The newly synthesized polymers are readily soluble in common organic solvents, such as THF, CHCl₃, and CH₂Cl₂, which is crucial for its purification and the deposition of high-quality film for efficient optoelectronic devices.^{6a} The number-average molecular weights (M_n) , the weight-average molecular weight (M_w) , and the polydispersity index (PDI) values of copolymers are listed in Table 1. $M_{\rm w}$ and PDI of the copolymers measured by GPC are $M_{\rm w} = 17240$ and PDI = 1.60 for **P1**, $M_w = 15790$ and PDI = 1.44 for **P2**, $M_w = 15780$ and PDI = 1.23 for **P3**, and $M_w = 17910$ and PDI = 1.78 for P4. As shown in Figure 1, the TGA curves indicate that the polymers have relatively high thermal stability without 5% weight loss before 320 °C, which can provide desirable thermal properties for practical applications.^{6b}

The absorption spectra of the copolymers **P1–P4** were measured in CH₂Cl₂ as shown in Figure 2 and Table 2. In the absorption spectra the following S0 \rightarrow S1 (π – π *) transitions appear at λ = 438 nm for **P1**, λ = 399 nm for **P2**, λ = 394 nm for **P3**, λ = and 475 nm for **P4**, and shorter wavelengths in the range of λ = 250–360 nm can be ascribed to the S0 \rightarrow S2 (π – π *) transition. Compared with **P1**, the



Figure 1 TGA curve of the four conjugated copolymers

Table 1 Molecular Weights and Thermal Properties of Copolymers

Polymer	Temp _{dec.} (°C) ^a	$M_{\rm n} ({\rm g/mol})^{\rm b}$	$M_{ m w}({ m g/mol})^{ m b}$	PDI
P1	350	10740	17240	1.60
P2	370	10920	15790	1.44
Р3	320	12850	15780	1.23
P4	410	10080	17910	1.78

^a Temperature of 5% weight loss measured by TGA in nitrogen.

^b Molar mass (M_n, M_w) and polydispersity index (PDI) were determined by GPC in THF against polystyrene standards with UV detection set at absorption maxima.

maximum absorption peak of the copolymer P3 shows an obvious red-shift (63 nm), which can be attributed to the introduction of two thiophenyl groups to the phenothiazine moiety. The similar results are obtained for P4 and P2.

1) Br(CH₂)₇Me

NaOH

2) Br₂, HBr

Table 2 Optoelectronic Properties and Fluorescent Quantum Yields(?) of Four Polymers $(1.0 \cdot 10^{-5} mol/L, CH_2Cl_2)$

Polymer	Absorption (nm)	Emission (nm)	Quantum yield (%)	HOMO (eV)	HUMO (eV)
P1	438	505	45 ^a	-5.23	-1.75
P2	399	473	38	-5.82	-2.09
P3	494	568	31	-4.96	-1.87
P4	475	528	40	-5.22	-2.00

The emissive wavelengths of four polymers are observed at $\lambda = 505$, 473, 568, and 528 nm for **P1**, **P2**, **P3**, and **P4**, respectively (Figure 3). When thiophene units are introduced into the main chain backbone, the emission peak of **P3** ($\lambda = 568$ nm), and **P4** ($\lambda = 528$ nm) are red-shifted by 63 nm and 55 nm, referred to **P1** and **P2**, respectively. It is also worth mentioning that introduction of the electrondeficient sulfone group into the conjugated polymer **P2** main chain backbone leads to obvious blue-shift (32 nm) for the emission wavelength. Four polymers have high quantum yields, such as 45% for **P1**, 38% for **P2**, 31% for **P3**, and 40% for **P4**, due to the effective intramolecular charge transfer between D and A units via the π -bridge linker.^{5a}

To further shed light on the electronic properties of four D- π -A-conjugated copolymers, computational studies of the molecular orbitals of their model compounds were carried out by using density functional theory (DFT) approaches at the B3LYP/6-31G (d, p) level. All the alkyl groups were replaced with an ethyl group to simplify the calculation. As is evident from Figure 4, the HOMO isosurfaces of all compounds show delocalization of the HOMO across the whole conjugated backbone structure,

Ċ₈H₁₇ M1





1)

Pd(PPh₃)₄, Cul

2

-Bi

Br

TMS

Pd(PPh₃)₂Cl₂, Cul

2) KOH, MeOH

Scheme 1 Synthesis procedures for the BTA-based conjugated polymers



Figure 2 UV-vis absorption spectra of P1, P2, P3, and P4 $(1.0 \cdot 10^{-5} \text{ mol } \text{L}^{-1} \text{ in } \text{CH}_2\text{Cl}_2)$

whereas the LUMOs are mainly localized on the acceptor core. Compared with model-1, model-2 shows its lower HOMO level, which can be attributed to the introduction of the strong electron-deficient sulfone group into the conjugated polymer P2 backbone. A smaller HOMO-LUMO band gap of model-1 than that of model-2 could be observed. The similar result can be found that model-3 has a lower band-gap energy (13.09 eV) than model-4 (3.22 eV). In addition, when thienyl units were introduced into the main-chain backbone of the conjugated poymers, model-3 and model-4 showed lower band-gap energies than **model-1** or **model-2**. Further, the calculation results of the model compounds show model-3 < model-4 < model-1 < model-2 in the HOMO–LUMO gap, which are excellently identical to the order of the absorption maxima of the UV-vis absorption in the order of P3 > P4 > P1 > P2.



Figure 3 Fluorescence spectra of P1, P2, P3, and P4

In summary, four 2-alkylbenzotriazole-based donor- π acceptor-type copolymers incorporating various donors in the main chain backbone could be synthesized via palladium-catalyzed Sonogashira coupling reaction and exhibit high fluorescence quantum yields with tunable band gaps. They are expected to be used as the potential optical materials.



Figure 4 HOMO and LUMO surface plots for model-1, model-2, model-3, and model-4

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References and Notes

- (a) Ozdemir, S.; Sendur, M.; Oktem, G.; Toppare, L. J. Mater. Chem. 2012, 22, 4687. (b) Oh, H. S.; Kim, T. D.; Koh, Y. H.; Lee, K. S.; Cho, S.; Cartwright, A.; Prasad, P. N. Chem. Commun. 2011, 47, 8931. (c) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Chem. Rev. 2007, 107, 1324.
 (d) Sirringhaus, H. Adv. Mater. 2005, 17, 2411. (e) Coakley, K. M.; McGehee, M. D. Chem. Mater. 2004, 16, 4533.
 (f) Zuniga, C. A.; Barlow, S.; Marder, S. R. Chem. Mater. 2011, 23, 658. (g) Sonar, P.; Williams, E. L.; Singh, S. P.; Dodabalapur, A. J. Mater. Chem. 2011, 21, 10532.
 (h) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. Angew. Chem. Int. Ed. 2008, 47, 4070.
- (2) (a) Tanimoto, A.; Yamamoto, T. *Macromolecules* 2006, *39*, 3546. (b) Brabec, C. J.; Dyakonov, V.; Scherf, U. In *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*; John Wiley and Sons: New York, 2008. (c) Forrest, S. R. *Nature* 2004, *428*, 911. (d) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A. *Nature* 2009, *457*, 679. (e) Kang, I.; An, T. K.; Hong, J. A.; Yun, H. J.; Kim, R.; Chung, D. S.; Park, C. E.; Kim, Y. H.; Kwon, S. K. *Adv. Mater.* 2013, *25*, 524.

- (3) (a) Kim, J.; Yun, M. H.; Anant, P.; Cho, S.; Jacob, J.; Kim, J. Y.; Yang, C. Chem. Eur. J. 2011, 17, 14681. (b) Taso, H. N.; Cho, D. M.; Park, I.; Hansen, M. R.; Mavrinskiy, A.; Yoon, D. Y.; Graf, R.; Pisula, W.; Spiess, H. W.; Mullen, K. J. Am. Chem. Soc. 2011, 133, 2605.
- (4) (a) Wang, M.; Hu, X. W.; Liu, P.; Li, W.; Gong, X.; Huang, F.; Cao, Y. J. Am. Chem. Soc. 2011, 13, 9638. (b) Zhou, E. J.; Cong, J. Z.; Tajima, K.; Hashimoto, K. Chem. Mater. 2010, 22, 4890. (c) Cui, C. H.; Fan, X.; Zhang, M. J.; Zhang, J.; Min, J.; Li, Y. F. Chem. Commun. 2011, 47, 11345. (d) Huo, L. J.; Hou, J. H.; Zhang, S. Q.; Chen, H. Y.; Yang, Y. Angew. Chem. Int. Ed. 2010, 122, 1542. (e) Bronstein, H.; Chen, Z. Y.; Ashraf, R. S.; Zhang, W. M.; Du, J. P.; Durrant, J. R.; Tuladhar, P. S.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos, T.; Sirringhaus, H.; Heeney, M.; McCulloch, I. J. Am. Chem. Soc. 2011, 133, 3272.
- (5) (a) Ma, X.; Mao, X. R.; Zhang, S. W.; Huang, X. B.; Cheng, Y. X.; Zhu, C. J. Polym. Chem. 2013, 4, 520. (b) Wu, Y. Z.; Ma, X.; Jiao, J. M.; Cheng, Y. X.; Zhu, C. J. Synlett 2012, 23, 778. (c) Wang, X. C.; Chen, S.; Sun, Y. P.; Zhang, M. J.; Li, Y. F.; Li, X. Y.; Wang, H. Q. Polym. Chem. 2011, 2, 2872. (d) Baek, N. S.; Hau, S. K.; Yip, H. L.; Acton, O.; Chen, K. S.; Jen, A. K. Y. Chem. Mater. 2008, 20, 5734. (e) Wang, X. C.; Sun, Y. P.; Chen, S.; Guo, X.; Zhang, M. J.; Li, X. Y.; Li, Y. F.; Wang, H. Q. Macromolecules 2012, 45, 1208. (f) Woo, C. H.; Beaujuge, P. M.; Holcombe, T. W.; Lee, O. P.; Fréchet, J. M. J. J. Am. Chem. Soc. 2010, 132, 15547. (g) Zhang, M. J.; Guo, X.; Li, Y. F. Macromolecules 2011, 44, 8798. (h) Bundgaard, E.; Krebs, F. C. Sol. Energy Mater. Sol. Cells 2007, 91, 954. (i) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. Chem. Rev. 2009, 109, 5868. (j) Chen, J.; Cao, Y. Acc. Chem. Res. 2009, 42, 1709. (k) Popere, B. C.; Pelle, A. M. D.; Thayumanavan, S. Macromolecules 2011, 44, 4767. (1) Duan, C. H.; Huang, F.; Cao, Y. J. Mater. Chem. 2012, 22, 10416.
- (6) (a) Patel, D. G.; Feng, F.; Ohnishi, Y. Y.; Abboud, K. A.; Hirata, S.; Schanze, K. S.; Reynolds, J. R. J. Am. Chem. Soc. 2012, 134, 2599. (b) Baran, D.; Balan, A.; Celebi, S.; Esteban, B. M.; Neugebauer, H.; Sariciftci, N. S.; Toppare, L. Chem. Mater. 2010, 22, 2978. (c) Hızalan, G.; Balan, A.; Baran, D.; Toppare, L. J. Mater. Chem. 2011, 21, 1804.
- (7) Zhang, Z. H.; Peng, B.; Liu, B.; Pan, C. Y.; Li, Y. F.; He, Y. H.; Zhou, K. C.; Zou, Y. P. Polym. Chem. 2010, 1, 1441.
- (8) Zhang, L. J.; He, C.; Chen, J. W.; Yuan, P.; Huang, L.; Zhang, C.; Cai, W. Z.; Liu, Z. T.; Cao, Y. Macromolecules 2010, 43, 9771.
- Price, S. C.; Stuart, A. C.; Yang, L. Q.; Zhou, H. X.; You, W. (9)J. Am. Chem. Soc. 2011, 133, 4625.
- (10) Peng, B.; Najari, A.; Liu, B.; Berrouard, P.; Gendron, D.; He, Y.; Zhou, K.; Zou, Y.; Leclerc, M. Macromol. Chem. Phys. 2010, 211, 2026.

- (11) Sang, G.; Zou, Y.; Li, Y. J. Phys. Chem. C 2008, 112, 12058.
- (12) Lee, J.; Lee, J. I.; Park, M. J.; Jung, Y. K.; Cho, N. S.; Cho, H. J. Hwang D. H.; Lee, S. K.; Park, J. H.; Hong, J.; Chu, H. Y.; Shim, H. K. Polym. Chem. 2007, 45, 1236.
- (13) Guerrero, M.; Urbano, M.; Velaparthi, S.; Zhao, J.; Schaeffer, M. T.; Brown, S.; Rosen, H.; Roberts, E. Bioorg. Med. Chem. Lett. 2011, 21, 3632.

(14) Synthesis Procedures for the BTA-Based Conjugated Polymers

Synthesis of P1

To a 100 mL Schlenk flask, M-1 (0.14 g, 0.05 mmol), M2 (0.31 g, 0.05 mmol), Pd(PPh₃)₄ (2.9 mg, 0.03 mmol), and CuI (0. 5 mg, 0.003 mmol) were added in 10 mL THF and Et₃N (6 mL) under N₂ atmosphere. The mixture was stirred at 90 °C for 2 d. The solvent was evaporated under vacuum after the mixture was cooled to r.t. The residue was dissolved and in CH_2Cl_2 (100 mL) and filtered; the filtrate was then concentrated and added to MeOH to precipitate the polymer. The polymer was dried in vacuum to give 210 mg of product in 58% yield. GPC results: $M_{\rm w} = 17240, M_{\rm p} = 10740$, PDI = 1.54. ¹H NMR (300 MHz, CDCl₃): δ = 7.24–7.21 (m, 6 H), 6.69–6.66 (m, 2 H), 3.77–3.76 (m, 4 H), 1.75–0.85 (m, 50 H). Anal. Calcd for (C48H64N4S)n: C, 78.85; H, 9.10; N, 7.66; S, 4.39. Found: C, 78.23; H, 9.16; N, 7.84; S, 4.27. Synthesis of P2

P2 was synthesized from monomers M-1 and M-3 in 70% yield by following in the same procedure used for the preparation of **P1**. GPC results: $M_{\rm w} = 17240$, $M_{\rm n} = 10050$, PDI = 1.72. ¹H NMR (300 MHz, CDCl₃): δ = 8.45–7.23 (m, 1 H), 8.21-8.19 (m, 2 H), 7.78-7.16 (m, 5 H), 4.80-4.76 (m, 2 H), 4.20-4.06 (m, 2 H), 1.21-0.85 (m, 50 H). Anal. Calcd for (C₄₈H₆₂N₄O₂S)_n: C, 75.55; H, 8.72; N, 7.34; S, 4.20. Found: C, 75.64; H, 8.63; N, 7.17; S, 4.28. Synthesis of P3

P3 was synthesized from monomers M1 and M4 in 73% yield by following the same procedure used for the preparation of **P1**. GPC results: $M_{\rm w} = 15780$, $M_{\rm p} = 12850$, PDI = 1.23. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.80-8.53$ (m, 2 H), 7.40-7.28 (m, 2 H), 7.12-6.81 (m, 6 H), 5.21-4.79 (br, 2 H), 3.83-3.81 (br, 2 H), 2.16-0.84 (m, 50 H). Anal. Calcd for: $(C_{56}H_{68}N_4S_3)_n$: C, 75.29; H, 7.67; N, 6.27; S, 10.77. Found: C, 75.18; H, 7.76; N, 6.12; S, 10.95. Synthesis of P4

P4 was synthesized from monomers M1 and M5 in 73% yield by following the same procedure used for the preparation of **P1**. GPC results: $M_{\rm w} = 17910$, $M_{\rm n} = 10080$, PDI = 1.78. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.34 - 8.32$ (m, 2 H), 7.84-7.83 (m, 2 H), 7.60-6.31 (m, 8 H), 4.80-4.82 (br, 2 H), 4.18-4.17 (br, 2 H), 2.26-0.59 (m, 50 H). Anal. Calcd for (C₅₆H₆₆N₄O₂S₃)_n: C, 72.69; H, 7.41; N, 6.05; O, 3.46; S, 10.40. Found: C, 72.76; H, 7.36; N, 6.01; O, 3.49; S, 10.37. Copyright of Synlett is the property of Georg Thieme Verlag Stuttgart and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.