

Synthesis and characterization of pyromellitic diimides-containing conjugated polymers

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Abstract Conjugated polymers based on pyromellitic diimides, the most compact aromatic tetracarboxylic diimides have been synthesized. Relatively low-lying LUMO energy levels and strong intermolecular interactions, together with solution processibility might enable them to become a promising new class of polymers for n-channel semiconducting materials.

Keywords Pyromellitic diimides · Naphthalene tetracarboxylic diimide · Perylene tetracarboxylic diimide · Stille polycondensation

Introduction

High mobility and air stable n-type organic semiconducting materials still pose big challenges in the field of organic electronics [1–3]. Recently, a lot of attentions have been focused on acene tetracarboxylic diimides [4]. So far, they have been considered as the most promising n-channel organic semiconducting materials for organic field-effect transistors (OFETs) applications [4–6]. Many naphthalene tetracarboxylic diimide (NDI) and perylene tetracarboxylic diimide (PDI) derivatives have been synthesized and have achieved high electron affinities, high electron mobilities, and, in some cases, air stabilities [7–19]. Conjugated polymers based on NDIs and PDIs as repeating units have also been studied extensively and have demonstrated as solution-processable electron transport materials [4, 6, 20].

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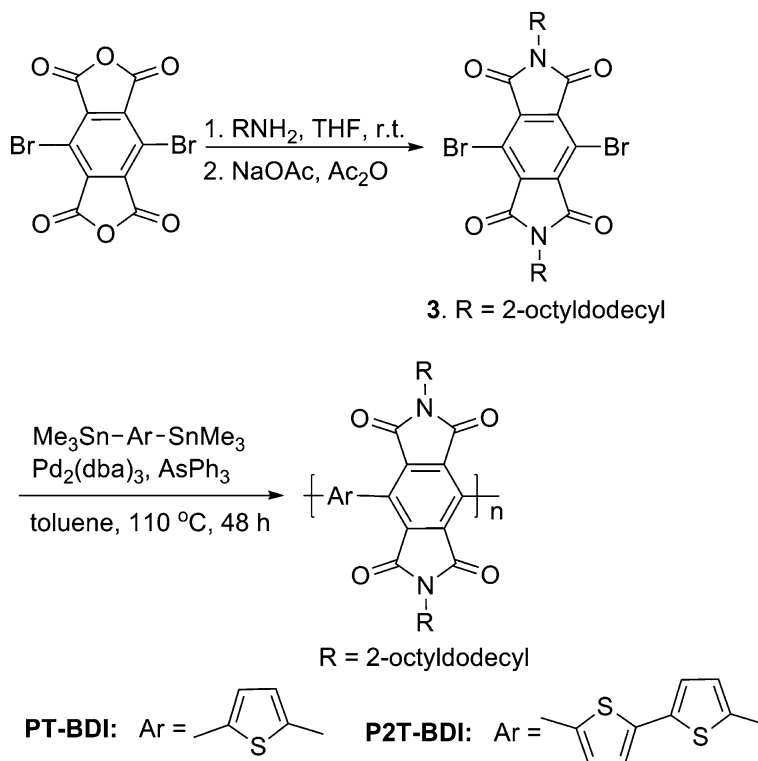
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Diimides of 1,2,4,5-benzenetetracarboxylic acid (pyromellitic diimides, **BDI**s) are the most compact aromatic tetracarboxylic diimides among acene tetracarboxylic diimides. It has shown promising properties as transparent n-channel organic thin-film transistors (OTFTs) with relative high mobility and good on/off ratios in OFET devices [21, 22]. **BDI** are well-known building blocks for polyimide dielectrics in polymer science and microelectronics. However, **BDI**-functionalized conjugated polymer has never been reported to the best of our knowledge. **BDI**-functionalized conjugated polymer might have some interesting electronic properties. It is well known that slight change on the core structures or substitutions of acene tetracarboxylic diimides can bring profound influence on the mobility and stability of devices. Significantly increasing devices environmental stability from PDI to NDI-functionalized polymers has been reported [4]. It is curious to know the effect of further reducing aromatic core size of acene tetracarboxylic diimides monomer on the HOMO/LUMO energy levels of resulted polymers and stability of devices based on those polymers. The extended conjugation in polymers might also overcome the relatively small aromatic core size of **BDI** monomer and result in better orbital overlap, therefore higher mobility. Here, we report the first synthesis of **BDI**-functionalized conjugated polymers and characterization of their electrochemical and photophysical properties. Preliminary electrochemical studies suggested that **BDI**-functionalized conjugated polymers are promising n-type organic materials.

Experimental

Synthesis and characterization

The detailed synthesis procedures, instrumentation, materials, NMR characterization of monomers and polymers, and DSC thermograms for the copolymers can be found in the supplementary material. The synthesis of monomer and the polymers was shown in Scheme 1. 3,6-Dibromopyromellitic dianhydride [23], 2,5-bis(trimethylstannyl)-thiophene (**1**) [24], and 2,5-bis(trimethylstannyl)-2,2'-bithiophene (**2**) [24] were synthesized according to the literature methods. The 2-octyldodecylamine was chosen to react with the dianhydride to ensure the solubility of the diimide monomer and **BDI**-functionalized conjugated polymers. The reaction was carried out through two-step procedure in one-pot to give *N,N'*-di-2-octyldodecyl-3,6-dibromopyromellitic diimide [25] in 60% yields. The polymer **PT-BDI** and **P2T-BDI** were synthesized by Stille polycondensation reactions with 1:1 monomer ratio of dibromide to distannane in the presence of tris(dibenzylideneacetone) dipalladium (Pd_2dba_3) as catalyst and triphenylarsine as ligand in toluene. Polymer **PT-BDI** was purified by precipitating in methanol and washing with methanol in a Soxhlet extractor for 24 h. And copolymer **P2T-BDI** was purified by precipitating in methanol and washing with methanol and hexane successively in a Soxhlet extractor for 24 h each. After removing solvent, **PT-BDI** and **P2T-BDI** were obtained as orange and red solid with yield of 96 and 72%. The polymers showed good solubility in common solvents, such as dichloromethane, chloroform,



Scheme 1 Synthesis of **BDI**-based conjugated polymers

chlorobenzene, and dichlorobenzene. The molecular weights of two polymers were measured by gel permeation chromatography (GPC) with polystyrenes as standards and tetrahydrofuran as eluent. The number-average molecular weights (M_n) were 26.2 and 20.4 kDa, and the polydispersity indexes were 1.68 and 2.29 for **PT-BDI** and **P2T-BDI**, respectively.

Results and discussion

Thermal analysis

The thermal stabilities of copolymers were investigated by thermogravimetric analysis (TGA). The point of 5% weight loss was selected as the onset decomposition point. The thermal decomposition temperatures (T_d) were 353 and 402 °C for **PT-BDI** and **P2T-BDI**, respectively. Two copolymers have adequate thermal stability for applications in OFETs and other optoelectronic devices. The DSC analysis was carried out to investigate the thermal transitions of the two polymers (Figure S1 and S2 in supplementary material). There were distinct exothermic peaks (at 98.5 °C for **PT-BDI** and at 178.3 °C for **P2T-BDI**) on the

cooling curves of the two copolymers; there were corresponding endothermic peaks (at 144.5 °C for **PT-BDI** and at 199.8 °C for **P2T-BDI**) on the heating curves of the two copolymers. The presence of prominent crystallization peaks indicated that new polymers had a strong tendency to crystallize in the solid state. Neither polymer displayed glass transition within the range of the study (20–300 °C).

Optical properties

The UV–vis absorption spectra of the polymers in chloroform solution and as thin films were shown in Fig. 1. The optical absorption properties of the copolymers were listed in Table 1. The absorption maxima of **PT-BDI** and **P2T-BDI** in solution were at 366 and 420 nm. The absorption maxima of **PT-BDI** and **P2T-BDI** solid films were at 401 and 479 nm. The thin-film absorption spectra of were broadened. Absorption spectra of polymers were red-shifted significantly from solution to thin film. The absorption maxima of **PT-BDI** and **P2T-BDI** were red-shift 35 and 59 nm from solution to film (Fig. 1). The significant red-shift indicated that strong intermolecular interactions and aggregation existed in the spin-coated thin solid films.

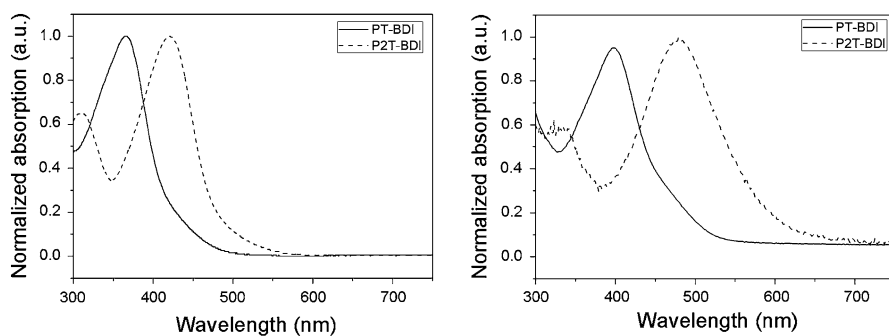


Fig. 1 Normalized UV–vis spectra of **PT-BDI** and **P2T-BDI** in chloroform solution (*left*) and as thin films (*right*)

Table 1 Optical and redox properties of **PT-BDI** and **P2T-BDI**

Polymers	Solution ^a λ (nm)	Film λ (nm)		E_g^{opt} (eV) ^b	E_{onset}^{red} (V)	LUMO (eV) ^c	HOMO (eV) ^d
	λ_{max}^{abs}	λ_{max}^{abs}	λ_{onset}^{abs}				
PT-BDI	366	401	546	2.27	−1.00	−3.70	−5.97
P2T-BDI	420	479	622	1.99	−0.90	−3.80	−5.79

^a In chloroform solution

^b Calculated from UV absorption spectrum of polymer films by the equation: Bandgap = 1240/ λ_{onset}^{abs}

^c LUMO = $-(4.70 + E_{onset}^{red})$

^d HOMO = $-(-LUMO + E_g^{opt})$

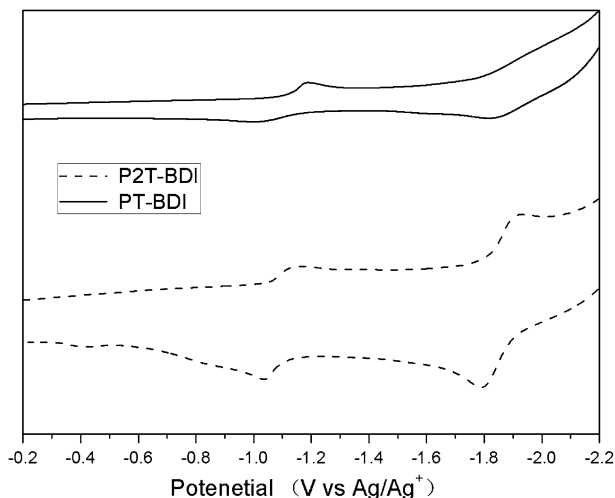


Fig. 2 Cyclic voltammograms of **BDI**-based copolymers thin films

Strong intermolecular π - π orbital interactions and ordered arrangements of polymers chains may exist in **PT-BDI** and **P2T-BDI** based on the information of crystallization transition on DSC and red-shift of film absorption spectra [26, 27]. These interactions and ordering may promote charge transport in OFET devices [28, 29]. The edges of the film absorption bands for **PT-BDI** and **P2T-BDI** were at 546 and 622 nm, respectively. The optical bandgaps (E_g^{opt}) were 2.27 eV for **PT-BDI**, 1.99 eV for **P2T-BDI** estimated from the absorption edges of solid-state films.

Electrochemical properties

The redox behaviors of the polymers (Fig. 2) were studied by cyclic voltammetry. The LUMO energy levels were calculated from the onset reduction potentials. They are -3.70 and -3.80 eV for **PT-BDI** and **P2T-BDI**, respectively. The relatively low-lying LUMO energy levels of the copolymers reflected the high intrinsic electron affinity of pyromellitic diimides. The LUMO levels of acene tetracarboxylic diimides-containing polymers were mainly determined by the acceptor units [30, 31]. Although the LUMO energy levels of new polymers were slightly higher than these of PDI and NDI alternating thiophene polymers (~ -3.9 eV) [4]. The LUMO energy levels of the new copolymers are still much below -3.0 eV for facilitating electron injection from electrodes.

Conclusion

In summary, the first synthesis of **BDI**-based conjugated polymers have been reported. The LUMO energy levels of polymers are very close to NDI-based counterparts. Strong intermolecular interactions and aggregation exist in these **BDI**

polymer thin films. Relatively low-lying LUMO energy levels and strong intermolecular interactions, together with solution processibility will enable them to become a promising new class of polymers for n-channel semiconducting materials.

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References

1. Newman CR, Frisbie CD, da Silva Filho DA, Bredas JL, Ewbank PC, Mann KR (2004) Introduction to organic thin film transistors and design of n-channel organic semiconductors. *Chem Mater* 16:4436–4451
2. Wen Y, Liu Y (2010) Recent progress in n-channel organic thin-film transistors. *Adv Mater* 22:1331–1345
3. Suzuki Y, Miyazaki E, Takimiya K (2010) ((Alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidal compounds: a new class of soluble n-channel organic semiconductors for air-stable organic field-effect transistors. *J Am Chem Soc* 132:10453–10466
4. Chen Z, Zheng Y, Yan H, Facchetti A (2009) Naphthalenedicarboximide- vs perylenedicarboximide-based copolymers. Synthesis and semiconducting properties in bottom-gate n-channel organic transistors. *J Am Chem Soc* 131:8–9
5. Huttner S, Sommer M, Thelakkat M (2008) N-type organic field effect transistors from perylene bisimide block copolymers and homopolymers. *Appl Phys Lett* 92:093302/1-3
6. Zhan X, Tan Z, Domercq B, An Z, Zhang X, Barlow S, Li Y, Zhu D, Kippelen B, Marder SR (2007) A high-mobility electron-transport polymer with broad absorption and its use in field-effect transistors and all-polymer solar cells. *J Am Chem Soc* 129:7246–7247
7. Katz HE, Lovinger AJ, Johnson J, Kloc C, Siegrist T, Li W, Lin YY, Dodabalapur A (2000) A soluble and air-stable organic semiconductor with high electron mobility. *Nature* 404:478–481
8. Katz HE, Johnson J, Lovinger AJ, Li W (2000) Naphthalenetetracarboxylic diimide-based n-channel transistor semiconductors: structural variation and thiol-enhanced gold contacts. *J Am Chem Soc* 122:7787–7792
9. Jones BA, Facchetti A, Marks TJ, Wasielewski MR (2007) Cyanonaphthalene diimide semiconductors for air-stable, flexible, and optically transparent n-channel field-effect transistors. *Chem Mater* 19:2703–2705
10. Shukla D, Nelson SF, Freeman DC, Rajeswaran M, Ahearn WG, Meyer DM, Carey JT (2008) Thin-film morphology control in naphthalene-diimide-based semiconductors: high mobility n-type semiconductor for organic thin-film transistors. *Chem Mater* 20:7486–7491
11. Jung BJ, Sun J, Lee T, Sarjeant A, Katz HE (2009) Low-temperature-processible, transparent, and air-operable n-channel fluorinated phenylethylated naphthalenetetracarboxylic diimide semiconductors applied to flexible transistors. *Chem Mater* 21:94–101
12. See KC, Landis C, Sarjeant A, Katz HE (2008) Easily synthesized naphthalene tetracarboxylic diimide semiconductors with high electron mobility in air. *Chem Mater* 20:3609–3616
13. Malenfant PRL, Dimitrakopoulos CD, Gelorme JD, Kosbar LL, Graham TO, Curioni A, Andreoni W (2002) N-type organic thin film transistor with high field effect mobility based on a *N,N'*-Dialkyl-3,4,9,10-perylene tetracarboxylic diimide derivative. *Appl Phys Lett* 80:2517–2519
14. Ahrens MJ, Fuller MJ, Wasielewski MR (2003) Cyanated perylene-3,4-dicarboximides and perylene-3,4:9,10-bis(dicarboximide): facile chromophoric oxidants for organic photonics and electronics. *Chem Mater* 15:2684–2686
15. Jones BA, Ahrens MJ, Yoon MH, Facchetti A, Marks TJ, Wasielewski MR (2004) High-mobility air-stable n-type semiconductors with processing versatility: dicyanoperylene-3,4:9,10-bis(dicarboximides). *Angew Chem Int Ed* 43:6363–6366
16. Ling MM, Erk P, Gomez M, Koenemann M, Locklin J, Bao Z (2007) Air-stable n-channel organic semiconductors base on perylene diimide derivatives without strong electron withdrawing groups. *Adv Mater* 19:1123–1127

17. Piliago C, Jarzab D, Gigli G, Chen Z, Facchetti A, Loi MA (2009) High electron mobility and ambient stability in solution-processed perylene-based organic field-effect transistors. *Adv Mater* 21:1573–1576
18. Molinari AS, Alves H, Chen Z, Facchetti A, Morpurgo AF (2009) High electron mobility in vacuum and ambient for PDIF-CN₂ single-crystal transistors. *J Am Chem Soc* 131:2462–2463
19. Jones BA, Facchetti A, Wasielewski MR, Marks TJ (2008) Effects of arylene diimide thin film growth conditions on n-channel OFET performance. *Adv Funct Mater* 18:1329–1339
20. Yan H, Chen Z, Zheng Y, Newman C, Quinn JR, Dotz F, Kastler M, Facchetti A (2009) A high-mobility electron-transporting polymer for printed transistors. *Nature* 457:679–686
21. Zheng Q, Huang J, Sarjeant A, Katz HE (2008) Pyromellitic diimides: minimal cores for high mobility n-channel transistor semiconductors. *J Am Chem Soc* 130:14410–14411
22. Carroll JB, Gray M, McMenimen KA, Hamilton DG, Rotello VM (2003) Redox modulation of benzene triimides and diimides via noncovalent interactions. *Org Lett* 5:3177–3180
23. Suh DH, Chung EY, Hong YT, Choi KY (1998) Synthesis of a novel poly(aryl ether) with pendent N-phenylimide groups. *Die Angewandte Makromolekulare Chemie* 254:33–38
24. Guo X, Watson MD (2008) Conjugated polymers from naphthalene bisimide. *Org Lett* 10:5333–5336
25. Kato S, Nonaka Y, Shimasaki T, Goto K, Shinmyozu T (2008) Novel pyromellitic diimide-Based macrocycle with a linear pi-electronic system and bis(phenylethynyl)pyromellitic diimide: syntheses, structures, photophysical properties, and redox characteristics. *J Org Chem* 73:4063–4075
26. Brisset H, Thobie-Gautier C, Jubault M, Gorgues A, Roncali J (1994) Small bandgap molecular semiconductors based on rigidified tetrathiafulvalene–bithiophene hybrid conjugated systems *J Chem Soc. Chem Commun* 1:1765–1766
27. Brisset H, Le Moustarder S, Blanchard P, Illien B, Riou A, Orduna J, Garin J, Roncali J (1997) Linearly extended hybrid tetrathiafulvalene analogues with bridged dithienylethylene- π -conjugating spacers. *J Mater Chem* 7:2027–2032
28. Zhan X, Facchetti A, Barlow S, Marks TJ, Ratner MA, Wasielewski MR, Marder SR (2011) Rylene and related diimides for organic electronics. *Adv Mater* 23:268–284
29. Zaumseil J, Sirringhaus H (2007) Electron and ambipolar transport in organic field-effect transistors. *Chem Rev* 107:1296–1323
30. Chen Z, Zheng Y, Yan H, Facchetti A (2009) Naphthalenedicarboximide- vs perylenedicarboximide-based copolymers. Synthesis and semiconducting properties in bottom-gate n-channel organic transistors. *J Am Chem Soc* 131:8–9
31. Durban MM, Kazarinoff PD, Luscombe CK (2010) Synthesis and characterization of thiophene-containing naphthalene diimide n-type copolymers for OFET applications. *Macromolecules* 43:6348–6352