Benzothiadiazole- and pyrrole-based polymers bearing thermally cleavable solubilizing groups as precursors for low bandgap polymers†

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We report the design, synthesis and characterization of new benzothiadiazole- and pyrrole-based copolymers whose solubility and bandgap drastically change after thermal treatment of their thin films.

Application of polymer-based solar cells is still limited by their moderate efficiencies, which result mainly from the small exciton diffusion length of most conjugated polymers.[1] This problem can be overcome in the bulk heterojunction solar cells, where the donor and acceptor materials are blended into bicontinuous structures.[2] However, these structures are difficult to predict and control. Another promising but relatively unexplored approach is to use resonance energy transfer to concentrate excitons near the donor/acceptor interface, as recently demonstrated on TiO₂/PTPTB/P3HT solar cells.[2] In these devices, a thin layer of poly-N-dodecyl-2,5-bis(2'-thienyl)pyrrole, 2,1,3-benzothiadiazole (PTPTB)[3] is placed between the primary absorbing layer, poly(3-hexyl)thiophene (P3HT), and the inorganic component, TiO₂. Directional energy transfer from P3HT to PTPTB helps to overcome the exciton-diffusion bottleneck, resulting in a three fold increase in the photocurrent.[2]

PTPTB[3] is one of the few low bandgap polymers to exhibit a relatively good stability to oxidation.[4] However, the high molecular weight fraction of PTPTB is soluble only in hot o-dichlorobenzene (ODCB). While this low solubility has limited the application of this polymer in electronic devices,[3,5] it allowed for the deposition of the layer of P3HT in these TiO₂/PTPTB/P3HT solar cells.[2] The fabrication of organic multilayer devices by low-cost deposition techniques, such as spin coating, requires the two polymers to have different solubility properties, which was exceptionally achieved in the previous example. Therefore, there is still a need for a more general method for the deposition of multiple layers of polymers.

Inspired by the solubility switch concept in chemically amplified photoresists,[6] as well as the recent work on thermally-removable solubilizing groups in semiconducting oligomers and polymers,[7–9] we designed new versions of PTPTB bearing secondary or tertiary carboester and carbamate protective groups. These functional groups are known to undergo thermolysis between 150 and 300 °C. Thus, the solubility of these polymers could be switched in a post-deposition treatment to give an insoluble polymeric layer, allowing

for the deposition of a second organic layer. We designed a modified version of PTPTB, **1**, by substituting the long alkyl chain with a carbamate protective group (Scheme 1). Thermal treatment of **1** is expected to give the insoluble polymer **2**. We also substituted the conjugated backbone in polymer **3** with tertiary carboester groups, which are known to improve the interaction with the titania interface once deprotected to carboxylic acid functionalities in **4**.[8]

Polymers **1** and **3** were obtained via Stille coupling reactions from monomeric precursors synthesized according to standard procedures (Scheme 2). An excess of the stannylated monomers (ca. 1.1 equivalent) versus the brominated monomers was necessary to obtain longer polymer chains. The crude polymerization products were fractionated via Soxhlet extraction using MeOH, hexanes, and acetone to first remove impurities and short oligomers, followed by THF to isolate the polymer. Size exclusion chromatography (SEC) in THF using polystyrene as a standard indicates that the two polymers have relatively high molecular masses (Mn = 11400 g mol⁻¹, PDI = 1.96 for **1**; Mn = 10200 g mol⁻¹, PDI = 2.23 for **3**), relatively to PTPTB,[3] resulting from better solubility brought by the branched alkyl chains. ¹H NMR in CDCl₃ confirms the expected ratios of the different monomer units.

Thermogravimetric analysis (TGA) of polymers **1** and **3** confirms the occurrence of the thermolysis reactions, as well as the good thermal stability of the deprotected polymers (Fig. 1). By TGA, polymer **1** exhibits a 35% mass loss (42% calcd) with an onset at 240 °C. Infrared spectroscopy before and after thermal treatment at 280 °C of a thin film of **1** confirms the predicted structure **2** (Scheme 1), with the complete loss of the carbamate protecting group apparent via the disappearance of the C–H and C=O stretching vibrations of the alkyl chains and carboester groups respectively, and the appearance of the N–H vibration (Fig. 2). Preliminary studies of the change in surface morphology of a thin film of **1** during thermal deprotection were conducted by atomic force microscopy. A film of **1** spin-coated on a titania substrate exhibits only a moderate increase in surface roughness, from 0.48 nm to 0.64 nm (root mean square roughness), after annealing at 240 °C for 30 min, suggesting that the film quality is not significantly compromised by the thermal deprotection process.[8]

Having demonstrated the thermal removal of the solubilizing groups, we were interested in studying the effect of this removal on the electronic properties of the polymeric films. These bulky groups probably affect the planarity of the polymeric backbone, which results in bandgaps higher than that of PTPTB, as observed by the blue shift of the absorption band of **1** in ODCB

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† Electronic supplementary information (ESI) available: Experimental section. See DOI: 10.1039/b601296p
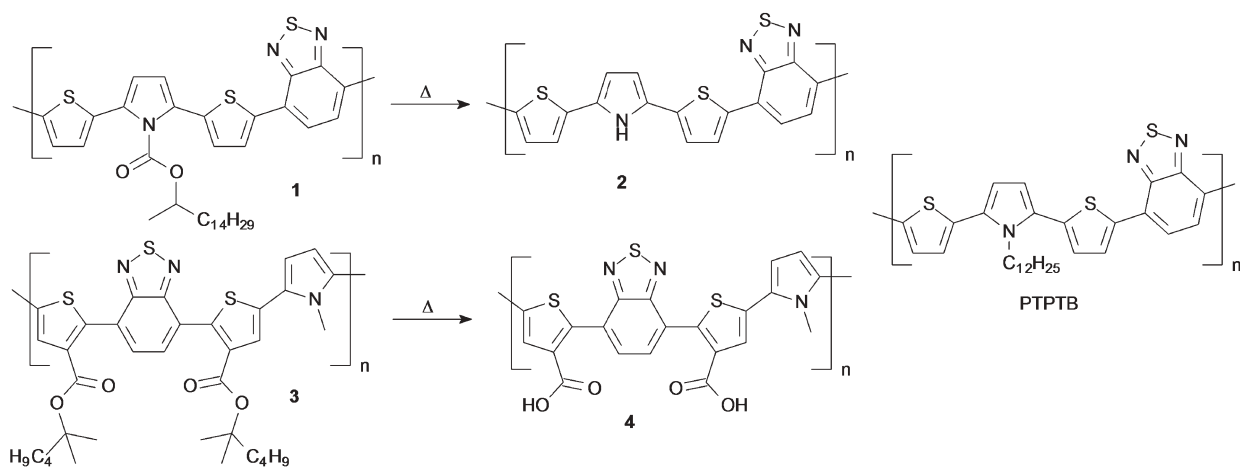
Scheme 1 Structures of polymers 1 and 3, their products of thermolysis, and PTPTB.
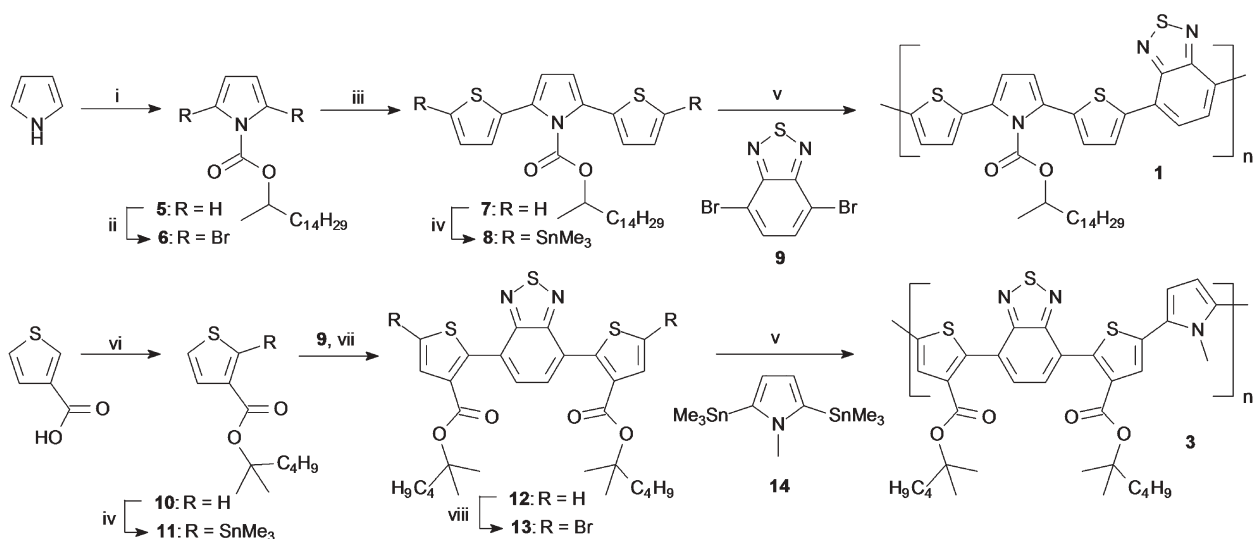
Scheme 2 Synthesis of polymers 1 and 3. (i) 1. NaH, THF. 2. 4-nitrophenyl(2-hexadecyl)carbonate (yield 81%). (ii) NBS, THF, −78 °C (94%). (iii) PdCl$_2$(PPh$_3$)$_2$, 2-(tributylstannyl)thiophene, THF, 60 °C (71%). (iv) 1. LDA, THF, −78 °C. 2. Me$_3$SnCl (91% for 8, 100% for 11). (v) PdCl$_2$(PPh$_3$)$_2$, THF, 60 °C. (vi) 2-methyl-2-hexanol, 2-chloro-3,5-dinitropyridine, pyridine, 115 °C (47%). (vii) PdCl$_2$(PPh$_3$)$_2$, THF/DMF, 60 °C (64%). (viii) 1,3-dibromo-5,5-dimethylhydantoin, DMF (71%).
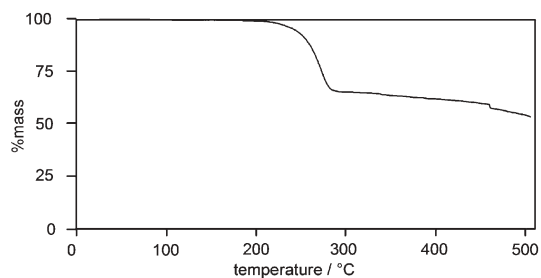
Fig. 1 Thermogravimetric analysis of 1, heating at 5 °C/min under inert atmosphere.

(λ_{max} = 590 nm for PTPTB,[3] λ_{max} = 540 nm for 1), and in thin films (λ_{max} = 655 nm for PTPTB,[3] λ_{max} = 580 nm for 1). The more important blue shift observed for 3 (λ_{max} = 460 nm in both ODCB and thin film) can be explained either by the strong steric effect of the tertiary carboesters, or by their electron-withdrawing effect

which alters the donor/acceptor nature of this alternating copolymer.

Cleavage of the solubilizing groups considerably modifies the optical properties of these polymers. This effect can be first visually confirmed by the strong color change observed while annealing the polymeric films: the color of 1 changes from purple to green, while 3 changes from red to purple. Thermal treatment of thin films of these polymers deposited onto glass substrates by drop-casting from a chloroform solution was followed by UV-Vis spectrometry (Fig. 3). Important shifts in the absorption bands toward lower energies were observed after annealing the films at temperatures at or above 280 °C for 30–60 min ($\Delta\lambda_{max}$ = 90 nm for 1 and 3). Removal of the bulky protective groups probably improves the planarity of the polymer backbones, increasing the effective conjugation length and thereby lowering the bandgap. The optical bandgap of a thin film of 1 was determined at 1.74 eV before annealing, and at 1.47 eV after thermal treatment, based on the onset of the absorption band. In polymer 3, the decrease of the

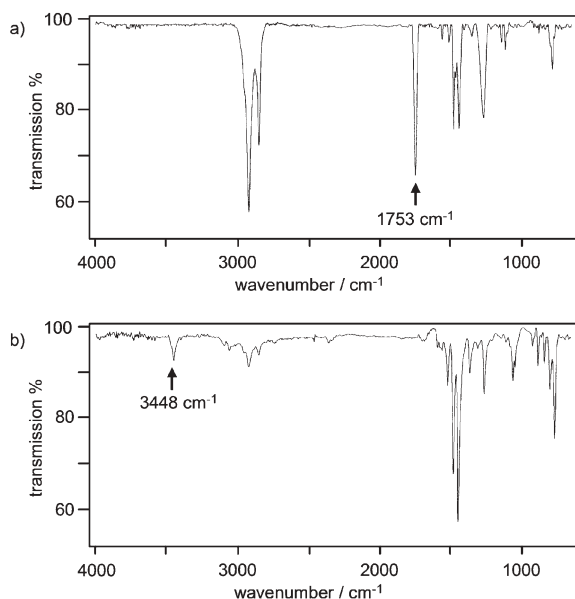**Fig. 2** Infrared spectrum of thin film of **1** on NaCl plate a) before, and b) after thermal treatment at 280 °C.
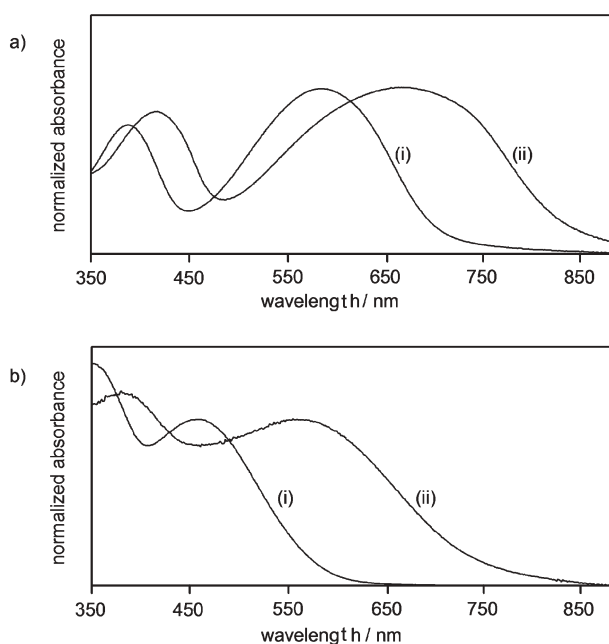

Fig. 3 Absorption spectra of thin films of a) **1**, and b) **3** drop-cast on glass from chloroform solution, before (i) and after (ii) thermal treatment for 1 h at 280–320 °C.

bandgap during the annealing process is even more significant, changing from 2.14 eV to 1.69 eV.

The reduction of the bandgap of these polymers after thermal treatment opens new perspectives in the design and synthesis of low bandgap polymers. Shifting the absorption properties of conjugated organic molecules to lower energy often gives rise to stability problems to oxidation. However, the present polymers

display a low bandgap only after post-processing treatment. Polymer **1** can be seen as a soluble percursor to a low bandgap polymer, making its manipulation during deposition easier due to its good solubility and stability. While displaying similar optical properties in its deprotected form to PTPTB, polymer **1** has the important advantage of good solubility in common organic solvents.

In summary, these benzothiadiazole- and pyrrole-based copolymers bearing thermally cleavable groups display numerous promising properties for application in photovoltaic devices. First, thermal removal of the alkyl chains imparts insolubility to the organic materials, allowing multiple depositions of polymeric thin films. Loss of the insulating solubilizing chains should also increase the hole mobilities[9] and absorption coefficients of these films, resulting in an improvement in the power conversion efficiency of organic-based solar cells. Application of these polymers in photovoltaic devices is currently under investigation in our laboratories. Finally, the higher stability of the protected polymer is expected to facilitate its manipulation during device fabrication.

Notes and references

1 (*a*) H. Hoppe and N. S. Sariciftci, *J. Mater. Res.*, 2004, **3519**, 1924; (*b*) K. M. Coakley and M. D. McGehee, *Chem. Mater.*, 2004, **16**, 4533.
2 Y. Liu, M. A. Summers, C. Edder, J. M. J. Fréchet and M. D. McGehee, *Adv. Mater.*, 2005, **17**, 2960.
3 (*a*) A. Dhanabalan, J. K. J. van Duren, P. A. van Hal, J. L. J. Van Dongen and R. A. J. Janssen, *Adv. Funct. Mater.*, 2001, **11**, 255; (*b*) C. J. Brabec, C. Winder, N. S. Sariciftci, J. C. Hummelen, A. Dhanabalan, P. A. Van Hal and R. A. J. Janssen, *Adv. Funct. Mater.*, 2002, **12**, 709.
4 (*a*) C. Winder and N. S. Sariciftci, *J. Mater. Chem.*, 2004, **14**, 1077; (*b*) M. R. Andersson, O. Thomas, W. Manno, M. Svensson, M. Theander and O. Inganäs, *J. Mater. Chem.*, 1999, **9**, 1933; (*c*) R. S. Loewe and R. D. McCullough, *Chem. Mater.*, 2000, **12**, 3214; (*d*) B. C. Thompson, Y.-G. Kin and J. R. Reynolds, *Macromolecules*, 2005, **38**, 5359.
5 J. E. Kroeze and T. J. Savenije, *Thin Solid Films*, 2004, **451-452**, 54.
6 (*a*) J. M. J. Fréchet, E. Eicher, C. G. Willson and H. Ito, *Polymer*, 1983, **24**, 995; (*b*) C. G. Willson, H. Ito, J. M. J. Fréchet, T. G. Tessier and F. M. Houlihan, *J. Electrochem. Soc.*, 1986, **133**, 181.
7 (*a*) J. H. Edwards, W. J. Feast and D. C. Bott, *Polymer*, 1984, **25**, 395; (*b*) B. Wessling, *Kunststoffe*, 1985, **i**, 375; (*c*) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539; (*d*) S. Son, A. Dodabalapur, A. J. Lovinger and M. E. Glavin, *Science*, 1995, **269**, 376; (*e*) G. A. Power, P. Hodge and N. B. McKeown, *Chem. Commun.*, 1996, 655; (*f*) P. Hodge, G. A. Power and M. A. Rabjohns, *Chem. Commun.*, 1997, 73; (*g*) P. T. Herwig and K. Müllen, *Adv. Mater.*, 1999, **11**, 480; (*h*) A. Afzali, C. D. Dimitrakopoulos and T. L. Breen, *J. Am. Chem. Soc.*, 2002, **124**, 8812; (*i*) A. Henckens, K. Colladet, S. Fourier, T. J. Cleij, L. Lutsen, J. Gelan and D. Vanderzande, *Macromolecules*, 2005, **3**, 19.
8 J. Liu, E. N. Kadnikova, Y. Liu, M. D. McGehee and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 9486.
9 A. R. Murphy, J. M. J. Fréchet, P. Chang, J. Lee and V. Subramanian, *J. Am. Chem. Soc.*, 2004, **126**, 1596.