Tetrahedron Letters 51 (2010) 6673–6676

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

New star-shaped molecules derived from thieno[3,2-*b*]thiophene unit and triphenylamine

N. Metri, X. Sallenave, L. Beouch, C. Plesse, F. Goubard *, C. Chevrot

Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), Université de Cergy-Pontoise, Institut des matériaux, 5 mail Gay-Lussac, Neuville-sur-Oise, 95031 Cergy-Pontoise Cedex, France

ARTICLE INFO

Article history:
Received 1 July 2010
Revised 12 October 2010
Accepted 13 October 2010
Available online 21 October 2010

Keywords:
Triphenylamine
Thieno[3,2-*b*]thiophene
Thiophene
Molecular glasses

ABSTRACT

A series of new substituted triphenylamine (TPA) derivatives with alkyl thieno[3,2-*b*]thiophene and thiophene units were synthesized in a combinatorial manner. Suzuki coupling of a dioxaborolane TPA derivative and 2-bromo-3-nonylthieno[3,2-*b*]thiophene or Stille coupling of fresh stannyl thieno[3,2-*b*]thiophene was used. All compounds were characterized by ^{1}H and ^{13}C NMR, HRMS, UV–vis spectrometry and DSC measurements. It was demonstrated that the optical and thermal properties of these materials can be tuned by varying both the conjugation length and thienothiophene and thiophene combination on the TPA branches. Moreover, the measured molar extinction coefficients were increasing from 63,000 (λ_{max} = 354 nm) to 131,000 L mol^{-1} cm^{-1} (λ_{max} = 428 nm) for TPA-thienothiophenes and TPA-bithiophene thienothiophenes, respectively. Some of them showed molecular glass behavior.

Among several organization states, amorphous molecular systems have constituted a new class of functional organic materials for use in various applications.[1–3] Despite their tendency to crystallization, small organic molecules can also form stable amorphous glasses above room temperature if their molecular structures are properly designed.[4] Among them, well-defined triphenylamine derivatives (TPA) have been studied intensively for their interesting physical properties, including good charge transport, electroluminescence, and improved thermal and morphological stabilities.[5,6] Recent studies of the synthesis of TPA derivatives having pseudo-three-dimensional conjugated architecture and their applications as advanced materials for photovoltaic systems[7–12] and organic light-emitting diodes[4,13,1] were carried out as well. Furthermore, the McCullough group has showed that the incorporation of heterocyclic thieno[3,2-*b*]thiophene into a polythiophene backbone led to the synthesis of polymers exhibiting charge carrier mobilities up to 0.15 cm^2/V with lifetimes of several months.[14] Indeed, the incorporation of rigid thieno[3,2-*b*]thiophene units in conjugated oligomers or polymers has been developed to improve their electronic properties and to optimize the performance of the corresponding devices.[15]

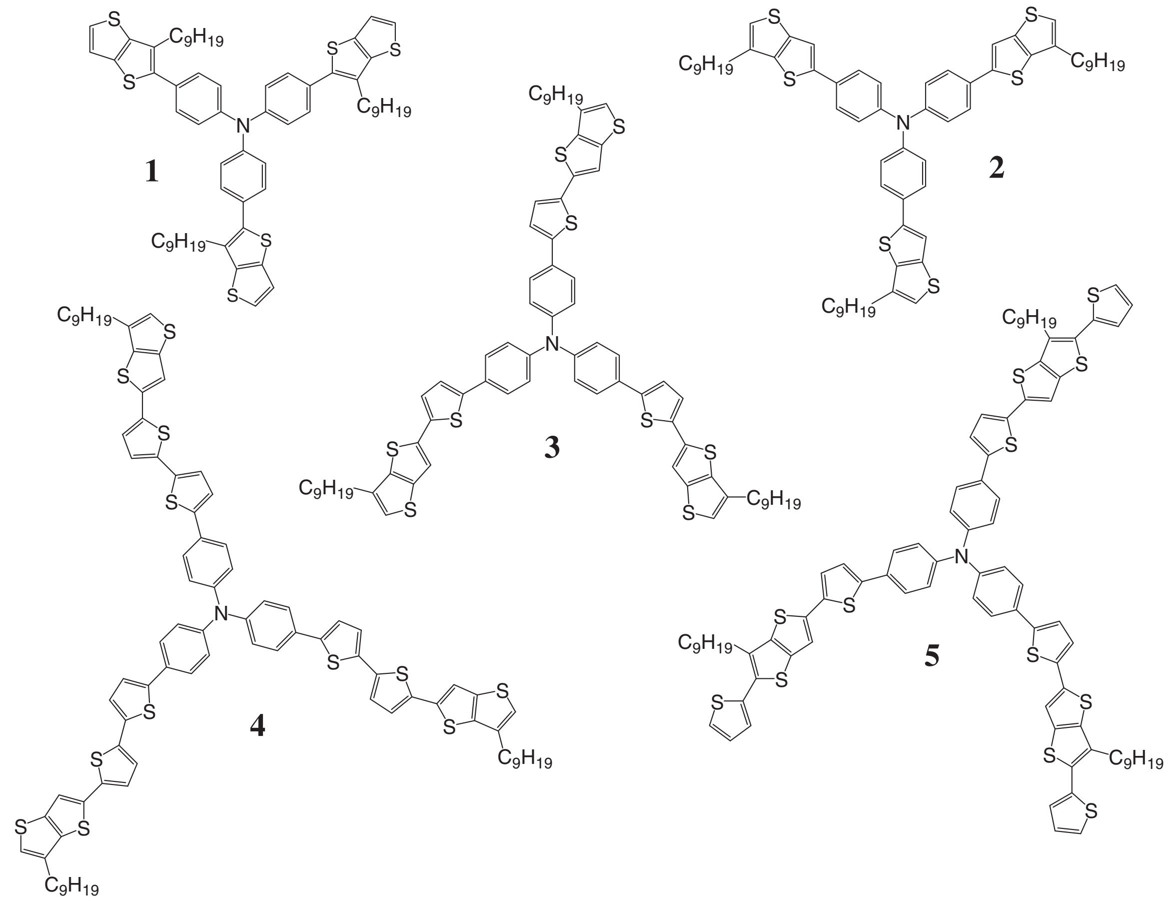
The original idea of the presented work was to combine both discussed approaches and to synthesize novel compounds having triphenylamine groups and thieno[3,2-*b*]thiophene moieties in one molecule. Thus, here we report the synthesis and the optical and thermal properties of a new series of five molecules **1–5** (Scheme 1) based on the TPA core derivatized with various combinations of alkyl thieno[3,2-*b*]thiophen/thiophene branches. Because of the higher degree of unsaturation in the fused rings, relatively long nonyl chains were used to increase the solubility of the resultant compounds **1**–**5** in different organic solvents, especially in chlorinated ones such as chloroform, chlorobenzene, or dichlorobenzene. The suggested structures differed in π-conjugated branch length and in the relative position of alkyl chain. It is noteworthy that in compound **1** the alkyl chain is located on the inner thiophene ring of the thieno[3,2-*b*]thiophen unit (named 'interior'), whereas in compounds **2–5** it is located on the outer ring of this unit (named 'exterior').

The synthetic routes for the different target molecules are outlined in Scheme 2. 3-Nonylthieno[3,2-*b*]thiophene, **6**, and 2-bromo-3-nonylthieno[3,2-*b*]thiophene, **8**, were prepared by following the synthetic methods similar to those described in Ref. 16 while molecules **10** and **11** by procedures close to Ref. 4. Two coupling methods were used according to the position of the alkyl chain relative to the TPA core. Compound **1** was synthesized via Suzuki coupling between the dioxaborolane derivative and 2-bromo-3-nonylthieno[3,2-*b*]thiophene **8** in 61% yield after column chromatography. To introduce the alkyl chain on the outer ring, Stille coupling was applied to obtain compound **2**. According to the reactivity of the different entities, two experimental conditions were used. For compound **2**, phenyl-thiophene coupling was achieved by the reaction of fresh stannyl thieno[3,2-*b*]thiophene **9**, and **7** with Pd(PPh$_3$)$_4$ as the catalyst in toluene at reflux. The resulting compound **2** was isolated in 62% yield.

---

* Corresponding author. Tel.: +33 134257022.
E-mail address: fabrice.goubard@u-cergy.fr (F. Goubard).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.10.082



Scheme 1. Molecular structure of compounds **1**–**5**.

A similar procedure was used to obtain molecules **10, 11.** and **5** from **7**, **10-Br,** and **3-Br**, respectively, It is necessary to mention that the isolated yields were quite high and varied in the range of 70–85% after precipitation. For coupling between two thiophene parts, the $Pd(PPh_3)_2Cl_2$ was used as the catalyst in THF at reflux. Such procedure was utilized for the preparation of compounds **3** and **4**. **10-Br**, **11-Br,** and **3-Br** were prepared by bromination of **10**, **11,** and **3**, respectively, with *N*-bromosuccinimide in a mixture of chloroform and acetic acid at room temperature.

Figure 1 shows the molar extinction coefficient spectra of **1** to **5** in $CHCl_3$ solution. The spectra of the oligothienyl-thienothiophene-triphenylamines, **2**, **3,** and **4**, revealed a progressive bathochromic shift of the absorption maximum with the increase of the conjugated system's length, from 386 (**2**) to 422 (**4**) nm, correspondingly. Simultaneously, the optical band gaps, which were determined from the lower-energy onset of the absorption band, gradually decreased from 2.99 to 2.53 eV (Table 1). At the same time the molar extinction coefficients were practically doubled in going from thienothiophene **2** to bithiophene thienothiophene **4** (Table 1, entries 2 and 4). This trend was found to be in accordance with a previously reported homologous series of conjugated oligothiophenes.[17–19]

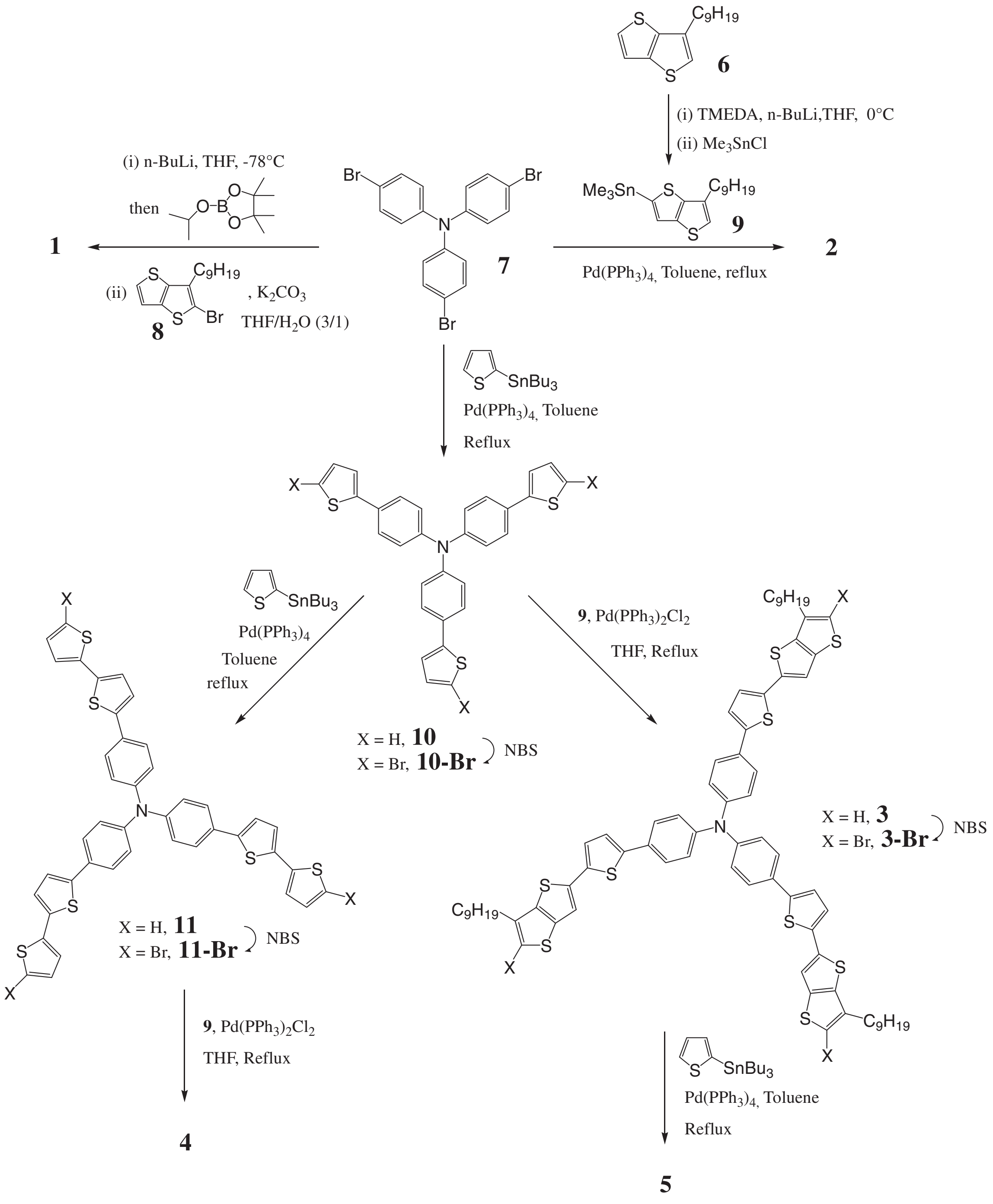
Compound **1** had the shortest λ_{max} of absorption among this group probably due to the deplanarization caused by the repulsive interactions between the nonyl chain and the phenyl group (Table 1, entry 1). Displacing the nonyl chain to the exterior position in compound **2** causes a lower deviation from planarity resulting in a bathochromic effect with an increase of 20% in absorption.

The high ε values (63,000–131,000 L mol^{-1} cm^{-1}) can be assigned to the combined effect of high molecular weights (>1000 g mol^{-1}) and of the presence of three conjugated branches per molecule.

Otherwise, the comparison of absorption signals for compounds **4** and **5**, containing the thienothiophene and thiophene units combined in a different order, revealed insignificant differences with a slight increases of λ_{max} and $\varepsilon_{\lambda max}$ for compound **5** probably due to greater planarity (Table 1, entries 4 and 5).

The thermal properties of all the compounds were examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under an argon atmosphere. The temperatures corresponding to 2% weight loss ($T_d^{2\%}$) and the glass transition temperatures (T_g), are summarized in Table 1. All compounds showed significant thermal stability, with $T_d^{2\%}$ values higher than 300 °C. Compound **4** demonstrated the lowest stability due to the presence of two adjacent thiophene rings (Table 1, entry 4). In contrast, compound **5**, with a thieno[3,2-*b*]thiophene unit between the thiophenes, exhibited the decomposition temperature as high as 444 °C. DSC analysis revealed that compounds **3** to **5** can be obtained as molecular glasses with glass transitions ranging from 27 to 57 °C.

In summary, synthesis, optical, and thermal properties of novel substituted thieno[3,2-*b*]thiophene molecules with triphenylamine core were investigated in detail. The synthetic method allowed the preparation of trisubstituted triphenylamine derivatives of thieno[3,2-*b*]thiophene and thiophene in a combinatorial manner starting from tris(4-bromophenyl)amine in relatively good yields. The newly suggested molecules (**1**–**5**) exhibited



Scheme 2. Synthetic routes of molecules **1–5**.

Table 1
Optical and thermal properties of star-shaped targets **1–5**

Compound	M^a (g mol^{-1})	λ_{max} (nm)	$\varepsilon_{\lambda max}$ (L mol^{-1} cm^{-1})	E_g (eV)	$T_g{}^b$ (°C)	$T_d^{2\%c}$ (°C)
1	1037	354	63,000	2.99	−3	361
2	1037	386	77,000	2.90	3	344
3	1283	396	106,000	2.65	27	354
4	1529	422	128,000	2.53	52	305
5	1529	428	131,000	2.53	57	444

[a] Molecular weight of the compound.

[b] Glass transition temperature is given according to DSC analysis with a heating rate of 20 °C/min.

[c] Temperature of 2 wt % loss according to TGA.

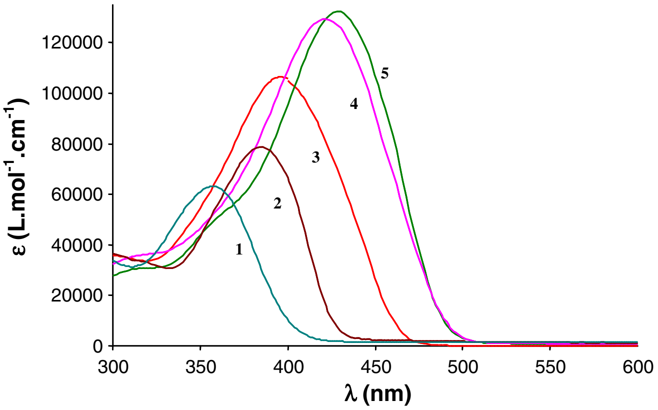


Figure 1. Molar extinction coefficient (ε) as a function of wavelength for the different thieno[3,2-*b*]thiophene-derivatized triphenylamines **1**–**5**.

extended π-conjugation with high molar extinction coefficients and some of them (**3**–**5**) demonstrated molecular glass behavior.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.082.

References and notes

1. Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75–93.
2. Strohriegl, P.; Grazulevicius, J. V. *Adv. Mater.* **2002**, *14*, 1439–1452.
3. Aich, R.; Tran-Van, F.; Goubard, F.; Beouch, L.; Michaleviciute, A.; Grazulevicius, J. V.; Ratier, B.; Chevrot, C. *Thin Solid Films* **2008**, *516*, 7260–7265.
4. Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.
5. Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. C. *Chem. Commun.* **2006**, 2245.
6. Karthikeyan, C. S.; Peter, K.; Wietasch, H.; Thelakkat, M. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 432–439.
7. Roquet, S.; Cravino, A.; Leriche, P.; Aleveque, O.; Frere, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459–3466.
8. He, C.; He, Q. G.; Yi, Y. P.; Wu, G. L.; Bai, F. L.; Shuai, Z. G.; Li, Y. F. *J. Mater. Chem.* **2008**, *18*, 4085–4090.
9. Roquet, S.; de Bettignies, R.; Leriche, P.; Cravino, A.; Roncali, J. *J. Mater. Chem.* **2006**, *16*, 3040–3045.
10. Cravino, A.; Roquet, S.; Aleveque, O.; Leriche, P.; Frere, P.; Roncali, J. *Chem. Mater.* **2006**, *18*, 2584–2590.
11. Aleveque, O.; Leriche, P.; Cocherel, N.; Frere, P.; Cravino, A.; Roncali, J. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1170–1174.
12. Roncali, J.; Leriche, P.; Cravino, A. *Adv. Mater.* **2007**, *19*, 2045–2060.
13. Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.
14. Heeney, M.; Bailey, C.; Genevicius, K.; Shkunov, K.; Sparrowe, D.; Tierney, S.; McCulloch, I. *J. Am. Chem. Soc.* **2005**, *127*, 1078–1079.
15. Turbiez, M.; Hergué, N.; Leriche, P.; Frère, P. *Tetrahedron Lett.* **2009**, *50*, 7148–7151.
16. Zhang, X. N.; Kohler, M.; Matzger, A. J. *Macromolecules* **2004**, *37*, 6306–6315.
17. Kirschbaum, T.; Azumi, R.; Mena-Osteritz, E.; Bäuerle, P. *New J. Chem.* **1999**, 241–250.
18. Diaz, A. F.; Crowley, J.; Bargon, J.; Gardini, G. P.; Torrance, J. B. *J. Electroanal. Chem.* **1981**, *121*, 355–362.
19. Thomas, K. R. J.; Hsu, Y. C.; Lin, J. T.; Lee, K. M.; Ho, K. C.; Lai, C. H.; Cheng, Y. M.; Chou, P. T. *Chem. Mater.* **2008**, *20*, 1830–1840.