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Tetrahedron Letters 47 (2006) 7089–7092
Tetrahedron Letters

Synthesis of novel star-shaped carbazole-functionalized triazatruxenes

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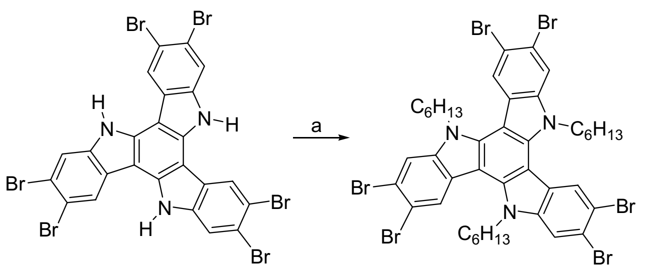
Received 17 May 2006; revised 17 July 2006; accepted 18 July 2006
Available online 10 August 2006

Abstract—The syntheses of novel well-defined star-shaped carbazole-functionalized triazatruxenes, which consist of six carbazole arms linked with a central triazatruxene core consisting of three carbazoles with one phenyl, are presented. Both 9-hexylcarbazole and 9-phenylcarbazole as arms gave high yields. Their chemical formulas were confirmed by means of ^{1}H NMR, MALDI-TOF mass spectroscopy, and elementary analysis. The fluorescent spectra showed that these compounds exhibit good blue fluorescence. The maximum fluorescence emission wavelengths were between 420 and 430 nm.

1. Introduction

During the past few years, the synthesis and application of carbazole derivatives has been of great interest for chemists and materials scientists due to their intrinsic photophysical and redox properties, i.e., they exhibit relatively intense luminescence and undergo reversible oxidation processes making them suitable as hole carriers.[1] Carbazole derivatives are also widely used as building blocks for potential organic semiconductors,[2] especially for organic light-emitting diodes.[3] Despite the huge amount of work already invested in these various applications, it is clear that further progress in these fields require intense research efforts focused on the design and synthesis of new compounds with electrochemical, optical, and electronic properties specifically tailored for each type of application.

Star-shaped oligomers with a central core have proven to be very useful in field-effect transistors, light-emitting diodes, and photovoltaic cells.[4] Star molecules consisting of linear molecular arms with a central core provide new electrical, optical, and morphological properties. Presently star-shaped conjugated architectures have attracted increasing attention as possible alternatives to linear conjugated oligomers. Fluorene or thiophene based truxene derivatives have been reported,[5] with only three-arms linked with the central truxene core. We recently described methods for the preparation of oligo-fluorene triazatruxenes.[6] In this letter, we describe the synthesis and characterization of novel star-shaped materials in which six short carbazole chains are connected to a central rigid triazatruxene core. In this structure, the triazatruxene core and chains are all



T0

Scheme 1. Synthesis of hexabromo-trihexyl-triazatruxene (**T0**). Reagents and conditions: (a) hexabromo-triazatruxene:1-bromohexane = 1:3.3, KOH, tetrabutyl ammonium bromide, DMSO, 100 °C.

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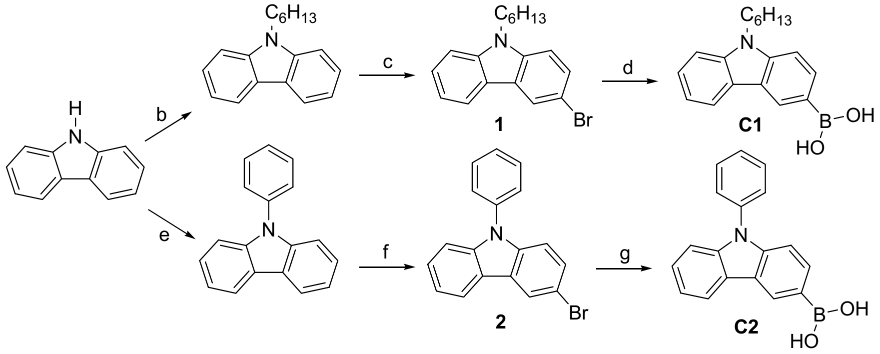
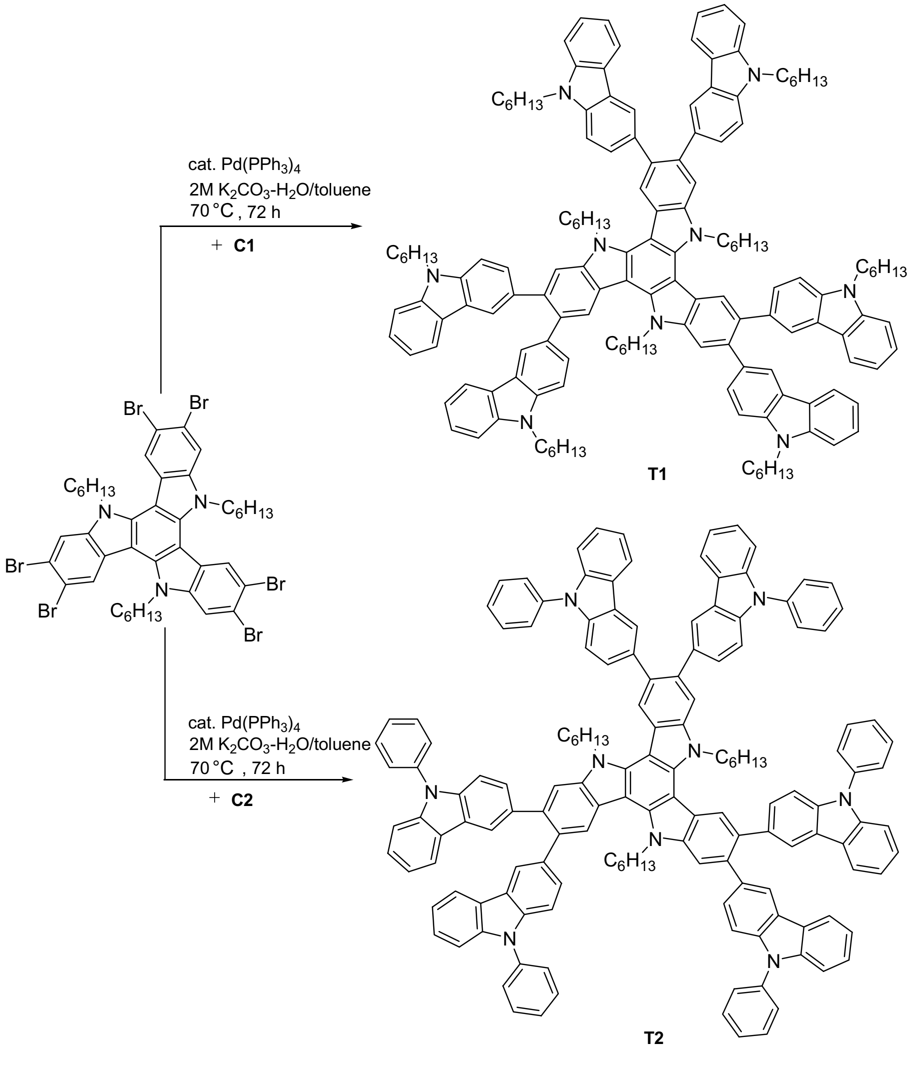
doi:10.1016/j.tetlet.2006.07.086

carbazoles. We consider such structures will have highly efficient hole transport ability, together with high thermal and electrochemical stability.

Carbazole arms were directly attached to the central triazatruxene core. For this purpose, at first, we synthesized triazatruxene according to the literature[6] and the



Scheme 2. Synthesis of carbazole-3-boronic acids **C1**–**C2**. Reagents and conditions: (b) carbazole:1-bromohexane = 1:1.1, KOH, tetrabutyl ammonium bromide, DMSO, 100 °C; (c) 9-hexyl-9*H*-carbazole:NBS = 1:1, DMF, dark, 0 °C; (d) *n*-BuLi (1.2 equiv), THF, −78 °C, (i-PrO)$_3$B (1.5 equiv), H_2O/HCl; (e) carbazole:1-iodobenzene = 1:1, K_2CO_3, CuI, 1,10-phenanthroline (0.1 equiv), *p*-xylene, 180 °C; (f) 9-phenyl-9*H*-carbazole:NBS = 1:1, DMF, 0 °C; (g) *n*-BuLi (1.2 equiv), THF, −78 °C, (i-PrO)$_3$B (1.5 equiv), H_2O/HCl.



Scheme 3. Suzuki cross-coupling route to **T1** and **T2** triazatruxene-carbazole oligomers.

hexabromo-triazatruxene core with hexyl terminal substituents, exploiting procedures similar to those described for alkylation of carbazole in the synthesis of 9-hexylcarbazole (Scheme 1).

In general, we used a repetitive procedure for the conversion of bromo derivatives **1**–**2** into the corresponding boronic acids **C1**–**C2** via lithiathion with *n*-BuLi, followed by quenching with triisopropyl borate and hydrolysis under acidic conditions (Scheme 2).

It is known that arylboronic acids form dimers through intermolecular hydrogen bonding or infinite networks in the case of polyfunctional boronic acids. As a result, OH protons are often 'invisible' in their ^{1}H NMR spectra. Moreover, they easily lose water, yielding the corresponding tricyclic anhydrides boroxines. Because the presence of water in the Suzuki cross-coupling reaction results in the hydrolysis of boronates back to the acids, the reactivity of both boronic acids and boronates are similar. In our case, arylboronic acids are protected with pinacol and then purified by flash chromatography on silica gel to give the pure products.

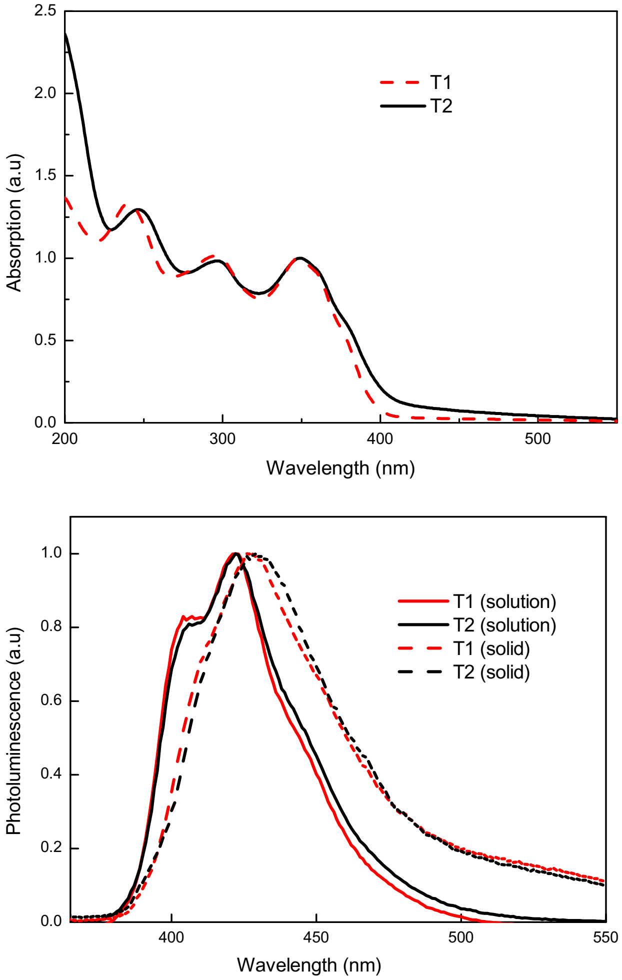


Figure 1. The UV–vis absorption and photoluminescence emission spectra of **T1**–**T2** in CH_2Cl_2 (ca. 10^{-5} mol/L) and in the solid state.

Table 1. Optical absorption and emission in CH_2Cl_2 solution and in the solid state

Compound	$\lambda_{abs,max}$ (nm)	$\lambda_{em,max}$ (nm, solution)	$\lambda_{em,max}$ (nm, solid)
T1	240, 295, 350	422	428
T2	248, 299, 350	422	428

For products **T1**–**T2**,[7] the carbazole moiety was introduced by C–C double-bond connection at its 3-position through a Suzuki cross-coupling of its boronate with hexabromo-triazatruxene derivative **T0** using $Pd(PPh_3)_4$ as the catalyst (Scheme 3). We also found that 9-hexylcarbazole and 9-phenylcarbazole gave similar high yields in syntheses of **T1** (53.2% yield) and **T2** (48.2% yield), however, the dissolution of **T1** was better than that of **T2**.

2. Optical properties

The optical properties of (**T1**–**T2**) were investigated by UV–vis absorption spectroscopy and photoluminescence spectroscopy in dichloromethane solution and in the solid state, respectively (Fig. 1). The spectral data are listed in Table 1.

The UV–vis spectra of **T1** and **T2** are shown in Figure 1. The absorption spectra of these carbazole derivatives exhibit the characteristic absorption peaks of carbazole unit between 240 and 350 nm. The absorption maximum of **T2** shows a small red-shift compared with that of **T1**. As shown in Figure 1, the emission spectra of **T1** and **T2** in dichloromethane solution (1×10^{-5} M) or in the solid state are nearly identical. **T1** or **T2** has a red-shift of 6 nm in the solid state compared with that in dichloromethane solution. This implies that interaction between **T1** or **T2** molecules exists in the ground state.

In summary, we have synthesized two novel star-shaped molecules with a triazatruxene core. By using N-alkylated and N-phenylated carbazole units as side arms of the novel molecules, we obtained materials with high solubility in common organic solvents. Moreover, their absorption and photoluminescence in CH_2Cl_2 solution were studied. They have different emitting maximum fluorescence wavelengths ranging from 420 to 430 nm which may be served as good blue light-emitting materials. The application of two novel star-shaped molecules with a triazatruxene core is under way in our laboratory.

Acknowledgments

This work was partially supported by the National Natural Science Foundation of China (Grants 60325412, 90406021, 50428303, 20172039, and 20472062), the Shanghai Commission of Science and Technology (Grants 03DZ11016 and 04XD14002), and the Shanghai Commission of Education under Grant 03SG03. The work was also supported by a research grant from the Innovation Project for graduate students of Jiangsu Province, the Key Laboratory of Organic Synthesis of

Jiangsu Province (No JSK008), the Natural Science Foundation of Jiangsu Province (No BK2004038 and BK2006048).

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7. *General procedure*: To a degassed (N_2) solution of hexabromo-trihexyltriazatruxene **T0** (1.00 g, 0.93 mmol) and $Pd(PPh_3)_4$ catalyst (0.45 g, 0.39 mmol) in toluene (30 mL), a solution of carbazole-boronic acid (8.37 mmol) in toluene (20 mL) and 2 M aqueous K_2CO_3 solution (10 mL) were added via syringe. The reaction mixture was stirred at 70 °C for 72 h. After cooling, the product was extracted with DCM, washed with water, and dried over $MgSO_4$. The solvent was evaporated, affording the crude mixture. Following column chromatography on silica gel eluting with PE–DCM (5:1), pure compound **T1**–**2** was obtained. *Tris(9-hexylcarbazol-3-yl)triazatruxene* (**T1**): yield (53.2%). Mp: 153–155 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.55 (s, 3H); 8.27 (s, 6H); 8.05 (t, $J = 7.8$ Hz, 6H); 7.82 (s, 3H); 7.46–7.33 (m, 18H); 7.21–7.14 (m, 12H); 5.12 (t, $J = 7.6$ Hz, 6H); 4.26–4.20 (m, 12H); 2.28–2.20 (m, 6H); 1.85–1.80 (m, 12H); 1.35–1.22 (m, 54H); 0.84 (t, $J = 7.4$ Hz, 18H); 0.73–0.69 (m, 9H). MALDI-TOF MS (*m*/*z*): calcd for $C_{150}H_{165}N_9$: 2092; found: 2092. (M^+), 2008 ($[M-C_6H_{12}]^+$). Anal. calcd for $C_{150}H_{165}N_9$: C, 86.04; H, 7.94; N, 6.02. Found: C, 85.98; H, 7.77; N, 6.14. *Tris(9-phenylcarbazol-3-yl)triazatruxene* (**T2**): yield (48.2%). Mp: 219.5–221 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.54 (s, 6H); 8.27 (s, 6H); 8.08 (t, $J = 8.0$ Hz, 6H); 7.80 (s, 3H); 7.63–7.50 (m, 21H); 7.42–7.32 (m, 21H); 7.26–7.21 (m, 15H); 5.3–5.07 (m, 6H); 2.34–2.23 (m, 6H); 1.56–1.03 (m, 18H); 0.88–0.78 (m, 9H). MALDI-TOF mass (*m*/*z*): calcd for $C_{150}H_{117}N_9$: 2043.94; found: 2044 (M^+), 1960 ($[M-C_6H_{12}]^+$). Anal. calcd for $C_{150}H_{117}N_9$: C, 88.07; H, 5.77; N, 6.16; found: C, 87.98; H, 5.69; N, 6.29.