Synthesis and Characterization of Starburst 9-Phenylcarbazole/Triazatruxene Hybrids

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Novel starburst triazatruxenes functionalized with six N-phenylated carbazole units have been synthesized and characterized. Good yields and high purity were readily obtained via an optimized microwave-enhanced six-fold Suzuki coupling methodology. High thermal stability and good amorphous properties as well as deep blue emissions (423–434 nm) were demonstrated. The introduction of six-substituted triazatruxene scaffolds could provide a new guideline for exploring novel solution-processable amorphous materials with dual functions for light-emitting and/or hole-transporting applications.

Carbazole derivatives[1] are playing an active role as key building blocks in the field of organic electronics, i.e. organic light-emitting diodes (OLEDs),[1–3] due to their intrinsic photophysical properties, good thermal stability, and hole-transport properties. They have also been recongnized as potential host materials for triplet emitters in OLEDs because of their tunable triplet energies and good carrier transporting characteristics.[4]

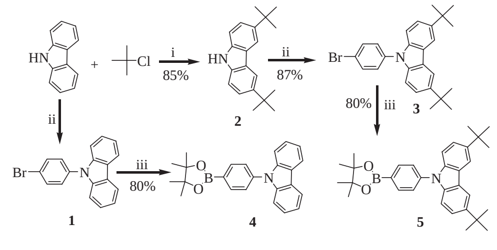
Star-shaped compounds consisting of a central core with radial linear conjugated arms have shown numerous promising advantages for thin-film device applications, including truly amorphous properties, well-defined size and structure, and high purity as well as the ease to fine-tune their physical properties via proper choice of the central core and conjugated arms.[5,6] Various kinds of star-shaped materials mainly based on three-substituted scaffolds with either a benzene, a 1,3,5-triphenylbenzene, a triphenylamino, or a triazine moiety as the core structure have been developed for light-emitting and/or charge-transporting applications.[5] In particular, carbazole-based star-shaped materials where carbazole units are used either as rigid core or radial arms exhibited interesting optoelectronic and redox properties.[3,5] Despite this progress, for improved amorphous properties and morphology stability, it would be interesting to explore more bulky and complex materials based on carbazole building blocks, yet it remains a challenge because of the synthetic difficulties.

We have recently developed a series of starburst triazatruxenes functionalized with oligofluorenes and have found them rather attractive for efficient light-emitting applications.[6] Here, we present the synthesis and characterization of a series of starburst 9-phenylcarbazole–triazatruxene hybrids in which six carbazole units are introduced to surround the rigid triazatruxene core via a phenyl bridge. The combination of carbazole periphery and the overlapped three-carbazole-fragment triazatruxene structure is expected to offer improved thermal and morphological stabilities and the dual functions for light-emitting and charge-transporting applications.

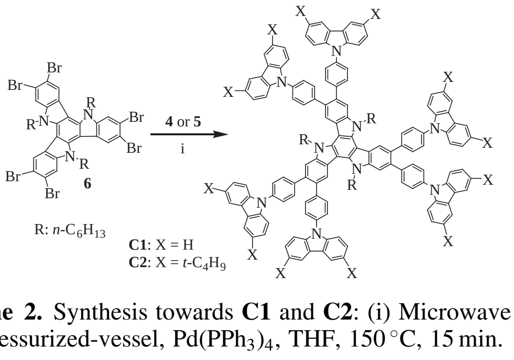
Triazatruxene core **6** was synthesized according to the procedures described in our previous work.[6] A modified Ullmann reaction was used to attach the phenyl bridge onto the nitrogen atom of carbazole to give the *N*-phenylcarbazole derivatives **1** and **3** in good yields (Scheme 1). CuI/L-proline proved to be an effective catalyst system for this reaction. Subsequent treatment of the above bromides with *n*-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave the corresponding boronic esters **4** or **5** efficiently.

Scheme 2 depicts the synthesis towards target molecules. An optimized microwave-enhanced multiple Suzuki coupling methodology[6b] was used to afford the two designed materials **C1** and **C2** with ideal yields (75.8 and 77% respectively) and high purity. It should be noted that such good yields and high purity were generally difficult to achieve under traditional conditions where partially substituted by-products are generally involved for such complex six-fold couplings and this presented serious challenges to separate the desired targets from those partially substituted counterparts.[6b]

C1 shows moderate solubility in THF and $CHCl_3$. With *t*-butyl chains on the 3,6-positions of carbazole units, **C2** is readily soluble in common solvents, such as CH_2Cl_2, $CHCl_3$, THF, toluene, etc. The structure and purity were confirmed by spectroscopic methods and elemental analysis. In MALDI-TOF mass spectrometry, the molecular peaks of **C1** and **C2** were



Scheme 1. Reagents and conditions: (i) $ZnCl_2$, CH_3NO_2, 5 h at room temperature. (ii) 1,4-Dibromo benzene, K_2CO_3, CuI, L-proline, DMSO, 140 °C. (iii) a) *n*-BuLi, −78 °C; b) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C to room temperature.



Scheme 2. Synthesis towards **C1** and **C2**: (i) Microwave heating, pressurized-vessel, $Pd(PPh_3)_4$, THF, 150 °C, 15 min.

Table 1. Physical properties of **C1**, **C2**, and **T1**[6a]

	$\lambda_{\rm abs}$/nm (THF)	$\lambda_{\rm em}$/nm (THF)	$\Phi_{\rm f}$ (THF)	$\lambda_{\rm abs}$/nm (film)	$\lambda_{\rm PL}$/nm (film)	$\Phi_{\rm f}$ (film)	$E_{\rm HOMO}$/eV	$E_{\rm LOMO}$/eV	$E_{\rm g}{}^{\rm CV}$/eV	$T_{\rm g}$/°C	$T_{\rm d}$/°C
C1	292.5, 344	423	0.65	295.5, 348.5	428	0.35	−5.35	−2.09	3.26	NA	442.9
C2	297, 345.5	423	0.68	298.5, 349.5	434	0.40	−5.34	−2.17	3.18	NA	438.1
T1	282, 348.5	429	0.72	289.5, 354.5	438	0.38	−5.16	−2.08	3.08	81.3	410.3

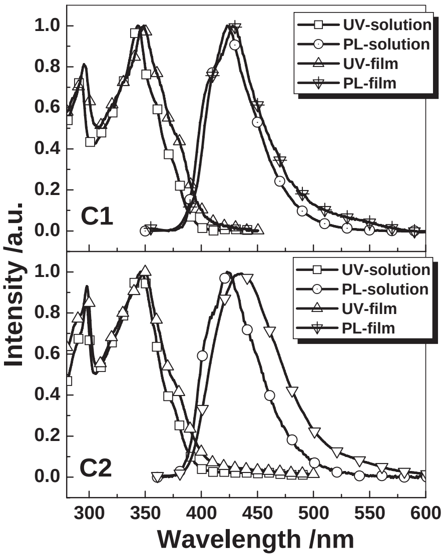


Figure 1. Absorption and PL spectra of **C1** and **C2** in THF and as films.

found at m/z 2044.7 (calcd MW: 2043.94) and at m/z 2718.4 (calcd MW: 2716.69), respectively, which agreed very well with the calculated values.

The UV–vis absorption and PL spectra of **C1** and **C2** in dilute tetrahydrofuran (THF) solution and in thin films are shown in Figure 1 and the photophysical data are summarized in Table 1. The absorption spectra of **C1** and **C2** were structureless with absorption peaks at 344 nm for **C1** and 345.5 nm for **C2** in THF solution. The absorption maxima at around 345 nm were attributed to a strong π–π^* transition. In film state, the absorption spectra of **C1** and **C2** remain almost identical with only 3–4.5 nm red shifts for the absorption maxima compared to those in dilute THF solution, suggesting suppressed molecular interactions in the ground state owing to the bulky starburst architectures. Although typical absorption peaks of carbazole units at around 290 nm can be clearly identified, no distinct characteristic absorption peaks of the triazatruxene core (peaks at 315.8, 256.2 nm in THF and peaks at 321 nm in solid state)[6c] were observed in the absorption spectra of **C1** and **C2** both in solution and in the solid state, implying efficient π-delocalization through the central triazatruxene core across the 9-phenylcarbazole arms. Both in solution and as films, **C1** and **C2** exhibit deep-blue fluorescence with an intense single emission peak ($\lambda_{\rm max}$) ranging at 423–434 nm and comparable quantum yields ($\Phi_{\rm f}$) relative to those of monofluorene-functionalized triazatruxene **T1**[6a] (Table 1).

Thermal and morphological properties of **C1** and **C2** were investigated by DSC and TGA studies (Table 1). The results are compared with those of **T1** to demonstrate the significance of incorporating carbazole functionality into the starburst molecular systems on improving the thermal and morphological stabilities. No distinct thermal processes were observed during the DSC scanning cycles from 20 to 250 °C for **C1** and **C2**, while a glass transition ($T_{\rm g} \approx 81.3$ °C) was determined for **T1** (Figure S6, Supporting Information). TGA study also showed much higher decomposition temperatures ($T_{\rm d}$) for **C1** and **C2** (442.9 and 438.1 °C, respectively), compared to that of **T1** (410.3 °C).

Due to the rich carbazole structure along with the electron-donating properties of triazatruxene,[6c] **C1** and **C2** exhibit relatively high HOMO energy levels (−5.35 and −5.34 eV respectively), which match well with the work function of ITO/PEDOT:PSS (−5.2 eV). These HOMO levels are even higher than general hole-transporting materials (TPD: −5.5 eV; NPB: −5.4 eV). Thus, good hole injection and transport ability can be expected when such materials are used as active materials in OLEDs.

In conclusion, novel starburst 9-phenylcarbazole/triazatruxene hybrids **C1** and **C2** were successfully synthesized and characterized. Deep blue emission ($\lambda_{\rm max}$, 423–434 nm) was obtained both in solution and as films. Good thermal stability and amorphous properties as well as proper HOMO energy levels and large band gaps (3.18–3.26 eV) suggest the potential of these starburst 9-phenylcarbazole/triazatruxene materials that are featured by rich carbazole units and unique 3D structures as promising light-emitting and/or hole-transporting materials as well as host materials for triplet emission.[7]

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