Microwave-enhanced multiple Suzuki couplings toward highly luminescent starburst monodisperse macromolecules†

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A facile and powerful microwave-enhanced multiple Suzuki coupling methodology has been developed and a novel series of highly luminescent six-arm monodisperse macromolecules have thus been prepared with high yield and purity.

Most recently, conjugated branched and dendritic macromolecules with a monodisperse nature and intrinsic two- or three-dimensional character have experienced an increasing interest due to their potential applications as active components in advanced materials.[1,2] In contrast to polymers and small organic molecules, these starburst compounds and dendrimers are characterized by superior structural uniformity and chemical purity as well as highly branched and dendritic structures, which are capable of preventing close packing and spatial reorientation of the molecules, thus suppressing self-aggregation[3a] and favoring the formation of high quality amorphous films.[3b] These unique features render this kind of material rather promising in achieving high-performance optoelectronics,[3] such as organic light-emitting diodes (OLEDs). However, their extensive applications are hampered by cumbersome and time-consuming preparation processes. Especially, performing the multiple transformations usually involved generally results in fairly low yield and remarkably difficult purification of the desired products from partially substituted by-products.[2a,4] Constructing these complex dendritic materials conveniently with high yield and purity is thus greatly challenging.

With the advance of dedicated microwave (MW) equipment, microwave-assisted organic synthesis (MAOS) has attracted widespread use and acceptance as a valuable alternative to the use of conductive heating in dramatically reducing reaction times (from days and hours to minutes and seconds).[5,6] Given the enormous literature precedents, many simple biaryl couplings[6a,d] and some polymerizations,[7] which mainly lead to linear compounds and can also be well achieved traditionally, can now be effectively accelerated by MW dielectric heating concomitant with improved product yields in many cases. Surprisingly, very few attempts have been made to investigate MW-assisted multiple couplings for starburst or multibranched compounds, which are not readily accessible using traditional methods.[2,4] In this communication, we report the first examples where a facile and powerful MW-enhanced multiple Suzuki coupling methodology has been developed and a novel series of highly luminescent six-arm monodisperse macromolecules **G1–G3** (Scheme 1, see ESI†) based on triazatruxene[8] and fluorene units have thus been prepared in minutes with high yield and purity. The relationship of their six-armed dendritic structures and optical properties has also been investigated.

The synthetic approach to desired materials is outlined in Scheme 1 in the ESI.† Oligofluorene bromides, as well as the corresponding boronates, have been obtained similarly to the procedures described in the literature.[2a,9] *N*-Alkylation of hexabromo-triazatruxene **1**[8] with 1-bromohexane afforded **2** yielding 92% in refluxing THF. Suzuki and Negishi couplings have been used in previous work to construct three-armed oligomers adopting conventional heating with some extent of success but still low yields and long reaction times (>5 days).[2a] We have therefore focused our attempts on developing MW-enhanced multiple coupling methodology (Table 1). As a starting point, we first studied the six-fold Suzuki couplings of **2** with **5** (Scheme 1, ESI†), as this would act as a sharpening stone for optimizing reaction conditions.

Selected optimization studies involved a variety of solvent systems and reaction parameters, such as time, applied power and reaction temperatures. The reactions were performed in 10 mL pressurized vessels which were filled under N_2 atmosphere using a computer-controlled monomode reactor.[10] We found that holding at 150 °C for 15 min in aqueous K_2CO_3–THF using $Pd(PPh_3)_4$ as a catalyst proved to be optimal reaction conditions for the six-fold transformations. A somewhat higher catalyst loading, however, turned out to be necessary because the precipitation of Pd black was fast under these conditions. Quite a high isolated yield (up to 89%) of desired product was obtained with a 1 : 7.8 molar ratio of **2** to **5**, using 0.6 equiv. $Pd(PPh_3)_4$, and 15.0 equiv. K_2CO_3.

After optimization of the general reaction parameters, in an attempt to broaden the scope of the MW-enhanced Pd-catalyzed

Table 1 MW-enhanced six-fold transformations toward **G1–G3**

Product	Molecular weight (M_w)	Reaction[a]	Hold time/min[b]	Yield[c]
G1	2593.0	**2** + **5**	15	89%
G2	4588.1	**2** + **7**	22	86%
G3	6583.2	**2** + **9**	30	84%

[a] Reactions were run in a sealed vessel. Conditions: **2** (1.0 equiv.), **5**, **7**, or **9** (7.8 equiv.), $Pd(PPh_3)_4$ (0.6 equiv.), aqueous K_2CO_3 (15.0 equiv.), THF. An initial microwave power of 100 W was used, the temperature being ramped from RT to 150 °C where it was then held until the corresponding hold time had elapsed. [b] Hold time at the set temperature. [c] Yield referring to the isolated amount of product.

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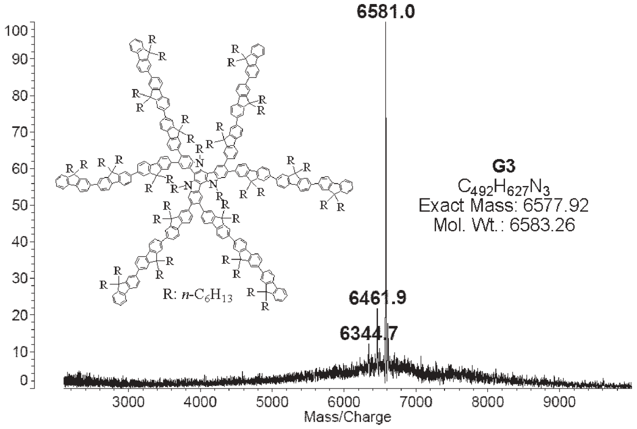

Fig. 1 MALDI-TOF mass spectrum of **G3**.

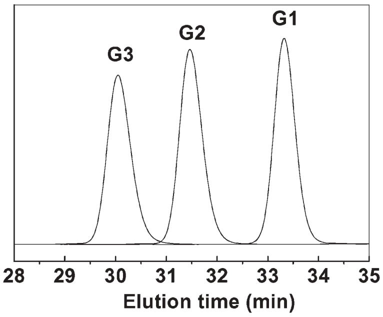

Fig. 2 GPC elution curves for triazatruxenes **G1**–**G3**.

multiple Suzuki couplings, we investigated the possibility of performing a wider range of reactions. Using this methodology, we also successfully coupled **2** with more steric boronic esters such as **7** and **9** in a very rapid manner. Note that these six-fold transformations showed completion under the same conditions described above except the hold times, which were then optimized as 22 and 30 min, respectively. The desired six-arm compounds were isolated by column chromatography on silica gel in excellent yields (**G2** 86%; **G3** 84%). Undoubtedly, the developed methodology is believed to be applicable to an even wider range.

We have also performed these multiple transformations using traditional methods,[2a,b] but this resulted in quite low yields and presented serious challenges during the separation of the desired products from partially substituted by-products, especially tetra- and penta-substituted by-products.

All new compounds have been adequately characterized by a combination of ^1H and ^{13}C NMR, as well as MALDI-TOF mass spectroscopy (MS). MALDI-TOF MS measurements were employed to characterize the precise structure, the molecular weight, and the purity. The results agreed with the calculated values very well as shown in Fig. 1 and ESI.† The propensity for the fully six-fold transformations is quite surprising considering steric factors. It was also further confirmed by gel permeation chromatography (GPC) analysis. As shown in Fig. 2, GPC elution curves for **G1**–**G3** exhibited a symmetrical narrow peak with a polydispersity of 1.01, which indicated a really high monodispersity and purity, and an absence of precursors and partially substituted by-products.

The absorption and photoluminescence (PL) spectra for **G1**, **G2**, and **G3** in dilute THF solutions are shown in Fig. 3. The photophysical properties are summarized in Table 2. Normally, **G1**, **G2**, and **G3** exhibit unstructured absorption bands that peak at 348.5, 360, and 366.5 nm, respectively, which are gradually red-shifted with increasing number of fluorene units (from 6 to 18) due to the increased conjugation length. Moreover, the absorption maxima are substantially red-shifted relative to those of the corresponding linear[9] or three-armed oligofluorenes.[2a,b] The results suggest that the π-delocalization system might be effectively extended through the triazatruxene core together with the increased branches to some extent. The UV-Vis absorption spectra of the starburst compounds **G1**–**G3** in films on quartz substrates are quite close to those in solutions except for slight red-shifts in the absorption maxima, as listed in Table 2.

We observe that the PL spectra of **G2** and **G3** in THF solutions are nearly identical as shown in Fig. 3, with emission maxima for both at 440 nm, which is 11 nm red-shifted relative to **G1** (429 nm). We may deduce that the emission has already been saturated for **G2**, although just two fluorene units are contained in each arm. We also observe that the PL maximum peaks in films of **G2** and **G3** (**G2** 439 nm; **G3** 437 nm) are quite close to those in solutions (both at 440 nm) but slightly blue-shifted (Fig. 4). This implies that the intermolecular interactions in the solid state are effectively suppressed and good amorphous states are formed in films for both **G2** and **G3**, which might be attributed to the novel six-arm dendritic hindered structure. Interestingly, both in solutions and in films, **G2**–**G3** exhibit none of the vibronic features usually observed in the spectra of

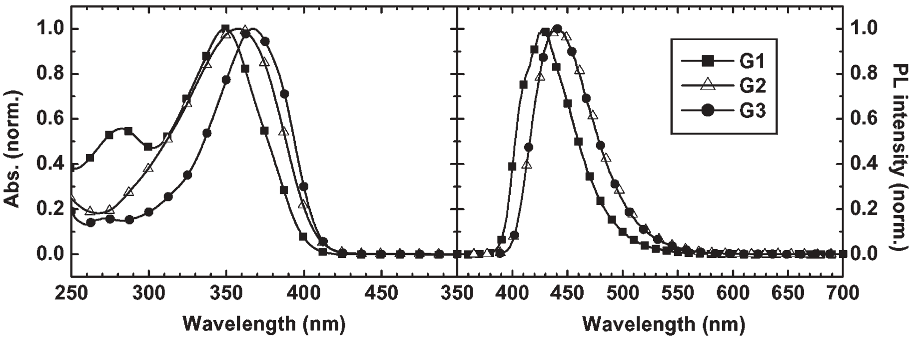

Fig. 3 Normalized absorption (left) and PL spectra (right) of **G1**–**G3** recorded in dilute THF (10^{-6} M) at room temperature. PL spectra were obtained upon excitation at the absorption maxima.

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Table 2 Photophysical properties of triazatruxenes **G1–G3**

		THF		Films		Φ_{PL}[a]	
Compound	M_w	λ_{abs}/nm	λ_{PL}/nm	λ_{abs}/nm	λ_{PL}/nm	THF	Films
G1	2593.0	282 sh, 348.5	429	289.5 sh, 354.5	438	0.72	0.38
G2	4588.1	360	440	366	439	0.85	0.73
G3	6583.2	366.5	440	372.5	437	0.88	0.75

[a] Estimated error in PL quantum efficiencies ~ ±10%. 9,10-diphenyl-anthracene (Φ_{PL} = 0.91 in ethanol) was used as standard.

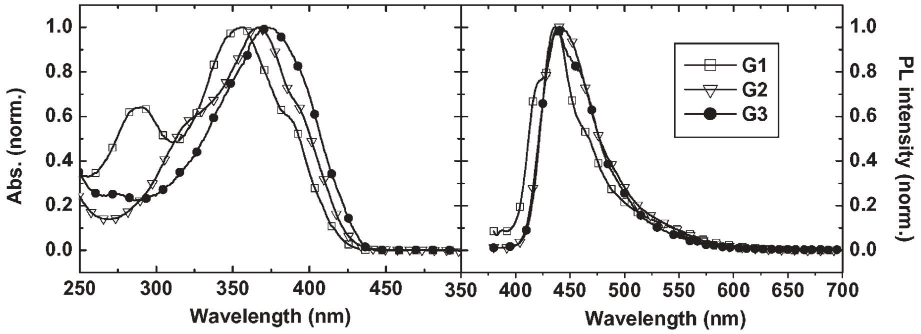

Fig. 4 Normalized absorption (left) and PL spectra (right) of **G1**–**G3** in film states at room temperature. PL spectra were obtained upon excitation at the absorption maxima.

oligo- and poly-fluorenes.[2,9,11] Furthermore, analysis of **G1**–**G3** by PL quantum efficiencies (Φ_{PL}) reveals that **G2** and **G3** are highly fluorescent materials with very efficient deep-blue emission (λ_{PL} = 437–440 nm) both in solution and in the solid state (Φ_{PL} are summarized in Table 2), indicating that they are rather promising blue light-emitting materials.

In summary, we have developed a facile and powerful MW-enhanced multiple Suzuki coupling methodology and a novel series of highly luminescent six-arm monodisperse triazatruxene derivatives **G1**–**G3** containing 6 to 18 fluorene units have thus been successfully prepared in minutes with high yield and purity. A preliminary investigation of the photophysical properties of the resulting compounds suggests that **G2** and **G3** are promising luminescent materials for high-performance blue OLEDs. The developed methodology is fast, convenient and powerful. It opens a new way to access well-defined conjugated functional dendritic materials conveniently with high yield and purity.

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