

Synthesis and Relationships between the Structures and Properties of Monodisperse Star-Shaped Oligofluorenes

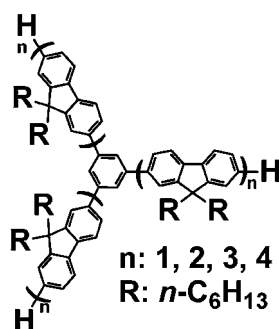
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ABSTRACT



A convenient approach to a series of star-shaped π -conjugated organic materials with oligofluorenes (OF) as the branches and a benzene ring as the core has been developed. The optical properties of these materials are liable to be tuned by introduction of more fluorene rings. The investigation of the structure–property relationship of these materials has indicated differences between star-shaped oligofluorenes and linear oligofluorenes, as well as polyfluorenes.

π -Conjugated organic materials with electronically rigid backbones have attracted considerable interest in both academic research and industrial applications due to increasing potential as active components for a wide range of electronic and optoelectronic devices.¹ Over the last few years, polyfluorene derivatives (PFs) have emerged as a promising class of blue-light-emitting conjugated polymers for use in polymer-based emissive displays because of high photoluminescent and electroluminescent yields, high hole mobility, as well as ease of property tunability through chemical structure modification and copolymerization.² However, devices are restricted by their tendency to form

aggregates³ and excimers⁴ or ketone defects^{2a,5} during either annealing or passage of current, leading to red-shifted and less efficient emission.

In comparison with these polymers, monodisperse conjugated oligomers possessing well-defined conjugation lengths

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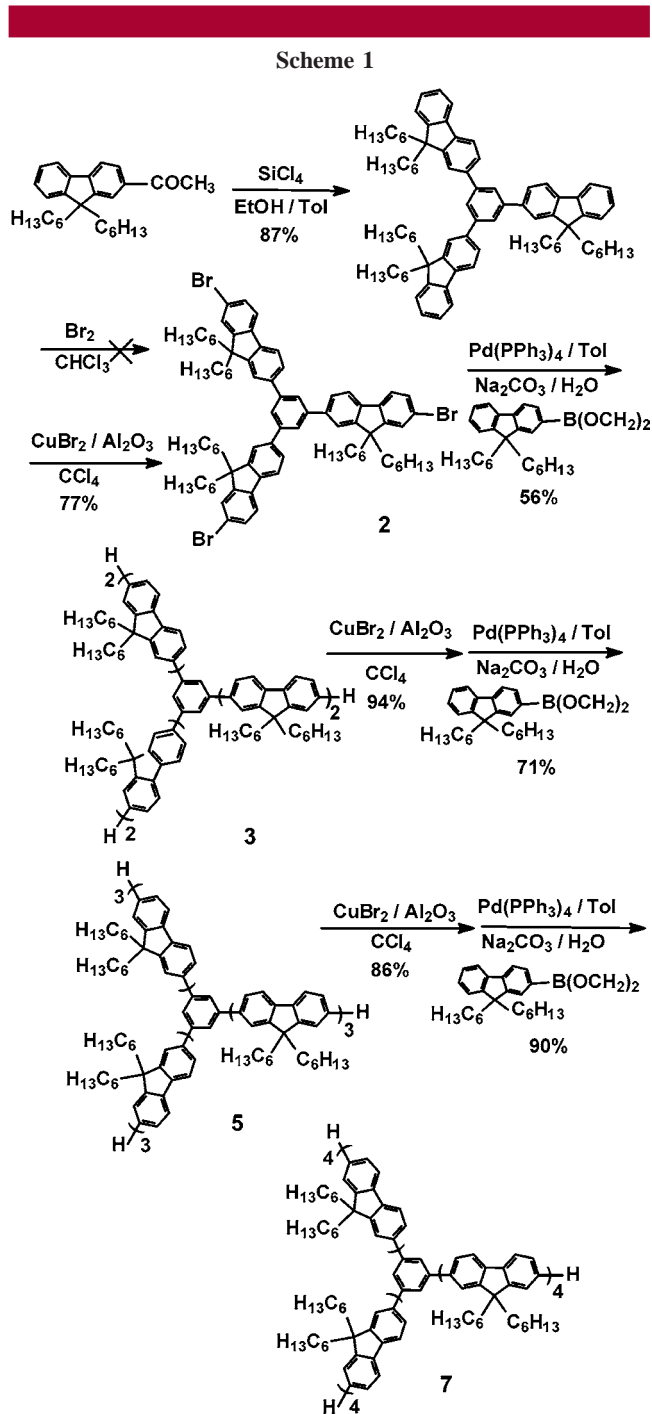
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and structures are characterized by structural uniformity, absence of chain defects, and ease of purification and characterization, which make them superior to conjugated polymers for a systematic investigation of structure–property relationships.⁶ For instance, a series of well-defined linear oligofluorenes were investigated to estimate their different effective conjugation lengths, which was highly variable for polymers in determining electronic properties such as band gaps, absorption coefficients, emission quantum yields, etc.⁷ Moreover, most recently, oligofluorenes have also acted as high-performance blue emitters for application in OLEDs.⁸ The morphological and thermal stability of oligofluorenes was substantially improved through introduction of aryl pendant groups,^{8a} or spiro-configured structures^{8b,c} while the electronic properties were retained. Modification of chemical structures with racemic or chiral alkyl groups even afforded monodisperse oligofluorenes exhibiting linearly or circularly polarized blue emission with good morphological stability and high glass transition temperatures (T_g).^{8e,f} Up to now, to the best of our knowledge, most of the oligofluorenes intensively investigated were linear rigid-rod molecules together with a few exceptions of spiro-linked examples possessing a three-dimensional (3D) structure. For the design of new material structures, C_3 symmetry confers very promising properties for nonlinear optics and electronic or optoelectronic devices.⁹

In this communication, we present a repetitive divergent synthetic strategy for preparing a series of well-defined star-shaped 1,3,5-tri(oligofluorenyl)benzene derivatives with C_3 symmetry, investigate structure–property relationships of materials, and also evaluate the absorption and emission properties of star-shaped oligofluorenes with linear ones.

The synthetic approach to the desired materials is illustrated in Scheme 1. The parent compound in this series, **1**, was synthesized in high yield via tetrachlorosilane-mediated cyclotrimerization of 9,9-dihexyl-2-acetylfluorene under solvents of ethanol and toluene.¹⁰ The bromination of **1** by employing bromine in chloroform failed to afford the desired **2**. ¹H NMR results showed that the bromination did not occur exclusively at 7-positions of fluorene rings, which results in great difficulty of getting pure **2** because of the similar polarity of the components in the mixture. Alumina-supported CuBr_2 selectively brominating aromatic hydrocarbons¹¹ under mild conditions successfully afforded the target molecule **2** with high yield. This method is feasible



for other larger compounds. Due to the convenience and high yields, palladium-catalyzed Suzuki cross-coupling reactions¹² were employed to achieve the growth of oligofluorene arms. **3** was readily obtained via cross-coupling between **2** and 9,9-dihexyl-2-fluorenylboronic ester. Repetitive bromination and cross-coupling reactions finally gave **7**, a monodisperse well-defined star-shaped derivative.

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Not only did we obtain appropriate ^1H and ^{13}C NMR and analytical data, we also employed MALDI-TOF/MS measurement to characterize the structure and molecular weight for new compounds. We also synthesized three linear oligo-(9,9-bis-*n*-hexylfluorene-2,7-diyl)s^{8f} (their structures are outlined in Supporting Information) to evaluate our star-shaped materials.

For compounds **1**, **3**, and **5**, after the bromination, the multiple signal arising between δ 7.30 and 7.40 ppm and belonging to the nine protons at 6-, 7-, and 8-positions of the outermost fluorene rings disappeared and a new multiple signal centered at about δ 7.50–7.47 ppm appeared, which was assigned to the six protons neighboring the bromine atoms. It was convenient to inspect the process of brominating and cross-coupling reactions through the change of these two characteristic signals in ^1H NMR spectra. With the increased π -electron delocalization and effective conjugation length of the whole molecule after the attachment of more fluorene segments, the specific single signal belonging to the protons of the benzene ring serving as the core gradually moved downfield, most apparently the chemical shift moving from δ 7.91 to δ 7.96 ppm for **3**. For the largest star-shaped compound **7**, poorly resolved multiple signals were observed ranging from δ 7.60 to 8.00 ppm, which was assigned to the proton of fluorene rings and those on the benzene ring. Due to the different local electron environment, the chemical shifts of the carbons at the 9-position of the fluorene rings in ^{13}C NMR spectra moved upfield in sequence from the innermost to the outermost fluorene ring, which also reflected the successful coupling and extension of the fluorene arms. For instance, the chemical shifts of these carbons for **5** were δ 55.43, 55.32, and 55.15 ppm, respectively.

The absorption and emission spectra of compounds **1**, **3**, **5**, and **7** in THF solution are shown in Figure 1. The

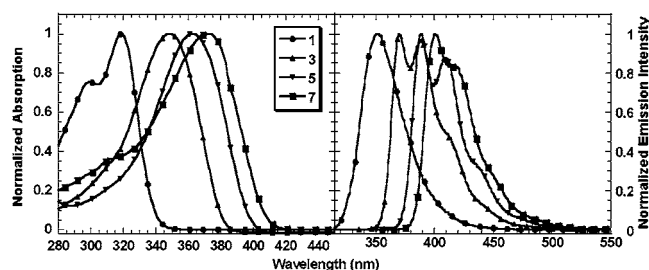


Figure 1. Absorption and emission spectra of oligomers **1**, **3**, **5**, and **7** in THF solutions at room temperature.

electronic absorption behavior of these star-shaped oligofluorenes exhibited a perfect correlation to the conjugation length, i.e., the absorption maximum was continuously red-shifted as the effective conjugated length of the respective oligofluorene branches increased. **1**, **3**, **5**, and **7** exhibited maximum absorptions at 319, 348, 363, and 372 nm, respectively, and were substantially red-shifted relative to the linear compounds of oligo(9,9-bis-*n*-hexylfluorene-2,7-

diyl)s (329 nm for the dimer, 352 nm for the trimer, and 364 nm for the tetramer). Such a red-shift may be due to the π -electron delocalization through the benzene core among the branches together with the contributions from the additional central phenyl ring. The electronic absorption maximum of **7** (372 nm) is quite close to that of poly(dialkylfluorene) (380 nm).¹³ Figure 2 shows the plot of the

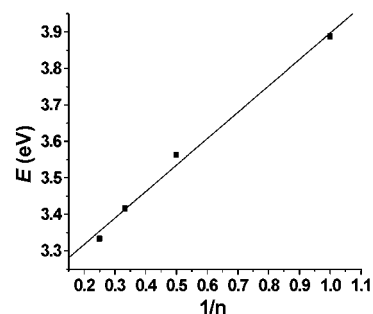


Figure 2. Energy (ΔE) of the lowest electronic transition for oligomers **1**, **3**, **5**, and **7** in THF solutions vs the inverse ring numbers ($1/n$) of oligofluorene in the conjugated homologue.

lowest energy transition vs the inverse ring numbers of oligofluorenes for the benzene core series in THF solution. The linear equations showed a saturation limit for ΔE vs the number (n) of fluorene rings.

$$E \text{ (eV)} = 3.17 + 0.72/n$$

The curve about the lowest energy transition vs the numbers of fluorene rings also suggested this trend. The photoluminescence (PL) features revealed typical characteristics of conjugated oligofluorenes derivatives. The emission maxima of the series were liable to be tuned by varying the number of the introduced fluorene rings, which was also red-shifted in comparison with the linear ones. The PL spectrum of **3** and **5** exhibited a maximum with a well-defined vibronic feature. However, it turned into a shoulder similar to that of polyfluorenes for compound **7**. Figure 3 exhibits absorption

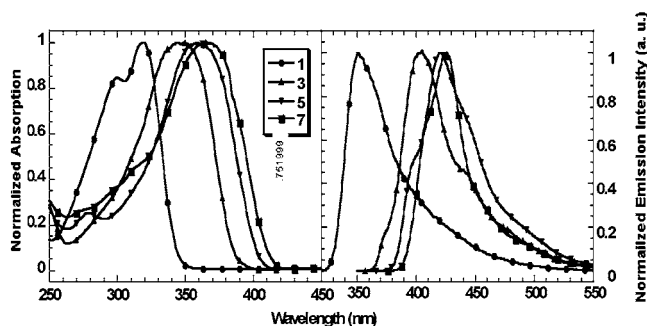


Figure 3. Absorption and emission spectra of oligomers **1**, **3**, **5**, and **7** in solid states at room temperature.

Table 1. Physical Properties of Star-Shaped Oligofluorenes Derivatives **1**, **3**, **5**, and **7**

oligomers	M_w	λ_{\max} abs (solutions)	λ_{\max} abs (films)	λ_{\max} PL (solutions)	λ_{\max} PL (films)	T_g ($^{\circ}\text{C}$)	band gap	Φ_f (THF)	Φ_f (films)
1	1075.1	319 nm	319 nm	352 nm	351 nm	35	3.49 eV	0.41	0.21
3	2071.4	348 nm	348 nm	370 (389) nm	402 nm	66	3.10 eV	0.63	0.34
5	3068.9	363 nm	359 nm	389 (410) nm	420 nm	76	3.02 eV	0.76	0.44
7	4065.8	372 nm	365 nm	402 (416) nm	426 nm	88	2.94 eV	0.85	0.56

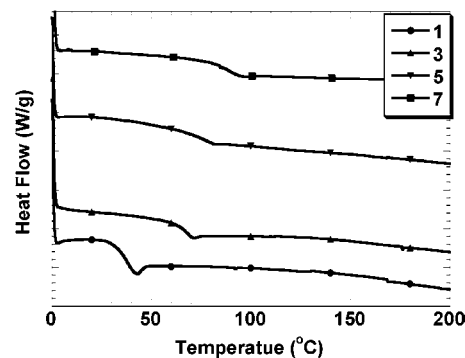
and emission spectra of **1**, **3**, **5**, and **7** in films spin-coated from toluene solutions. In comparison with PL spectra in solutions, PL spectra of derivatives **3**, **5**, and **7** in films are obviously red-shifted, although the absorption spectra exhibited a small blue-shift; however, we observed the same absorption and emission maxima of **1** both in solutions and in solid states. Moreover, **7** did not exhibit any of the vibronic features at 444 and 476 nm usually observed in spectra of polyfluorenes.

For photoelectronic applications, the thermal stability of organic materials is critical for device stability and lifetime. The degradation of organic photoelectronic devices depends on morphological changes resulting from the thermal instability of the amorphous organic layer.¹⁴ The morphological change might be promoted by the rapid molecular motion near the glass transition temperature (T_g). All compounds exhibited an onset of evaporation or decomposition at temperatures greater than 350 $^{\circ}\text{C}$ with no weight loss at lower temperatures. Compounds were in an amorphous state at room temperature. The glass transition temperatures were improved from 35 (oligomer **1**) to 88 $^{\circ}\text{C}$ (oligomer **7**) with an increase of fluorene rings at every branch, which was close to that of poly(9,9-dialkylfluorenes).¹³ Table 1 also summarizes temperatures of glass transitions (T_g) of **1**, **3**, **5**, and **7**. We observed that the compounds formed kinetically stable amorphous phases after thermal annealing. Accordingly, pristine samples typically showed a weak and broad melting endothermic peak on the first heating cycle of the DSC experiment. Once residual solvents in samples were removed, only amorphous phases of most compounds were observed and no recrystallization and melting peak was observed upon heating above the glass transition temperature (T_g). Typically differential scanning calorimetric thermogram characteristics of **1**, **3**, **5**, and **7** are shown in Figure 4 for elucidation.

In summary, we have presented a convenient and efficient approach to soluble star-shaped 1,3,5-tri(oligofluorenyl)-

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**Figure 4.** DSC curves (second run) of oligomers **1**, **3**, **5**, and **7**.

benzene derivatives with C_3 -symmetry. We have provided a facile method of selective bromination for 1,3,5-tri(oligofluorenyl)benzene derivatives. These bromides might serve as good building blocks for the construction of fluorene-based starburst or dendritic molecules. The Suzuki cross-coupling reactions successfully achieve the extension of oligofluorene branches with excellent yields. The absorption and emission spectra of these materials in THF solutions and in solid states are readily tuned by varying the number of the fluorene rings. The investigation of photo properties indicates that **7** not only exhibits the narrow emission spectra but also has structureless features in solid states due to the star-shaped structure, which may be helpful for the systematic investigation of structure–property relationships on the design of novel and efficient organic optoelectronic materials.

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Supporting Information Available: Experimental procedures and additional data and details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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