Synthesis and Characterization of Novel Monodisperse Starburst Oligo(fluoreneethynylene) Based on Truxene Moiety

Qing-Quan Chen,[1] Feng Liu,[1] Zhun Ma,[1] Bo Peng,[1] Wei Wei,*[1] and Wei Huang*[2]
[1]*State Key Laboratory for Advanced Photonic Materials & Devices, Fudan University, Shanghai 200433, P. R. China*
[2]*Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications, Nanjing 210003, P. R. China*

(Received November 1, 2007; CL-071204; E-mail: iamww@fudan.edu.cn, wei-huang@njupt.edu.cn)

A series of novel monodisperse star-shaped oligo(fluorene-ethynylene)s, which contain hexahexyltruxene as the central core linked with oligo(fluoreneethynylene) as the arms, are presented.

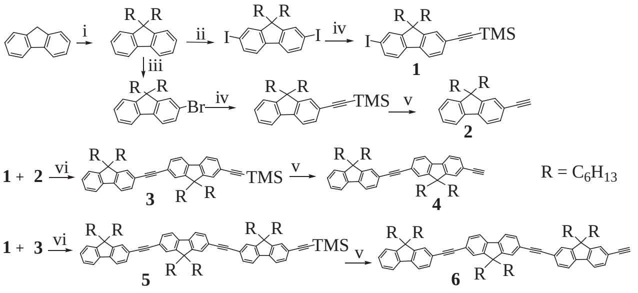
Poly(aryleneethynylene)s (PAE) are important conjugated materials, widely used in advanced biodetection schemes,[1] light-emitting diodes,[2] and transistor-type applications,[3] by virtues of their high fluorescence quantum yield and excellent stability, and easily synthesized by either the Heck–Cassar–Sonogashira coupling or by alkyne metathesis.[4] As a general matter, the photophysical properties of PAEs are critically dependent upon chain ordering, conformation and selection of suitable aromatic building blocks.[5]

Recently, charge-transporting dendrimers, as an important class of organic semiconducting material,[6] have become increasingly important as the active component for use in various applications.[7] The truxene moiety, by virtue of its unique three-dimensional topology, is an attractive building motif for use as potential dendrimer building block via readily available functionalization at C-2, C-7, C-12-positions and C-5, C-10, C-15-positions respectively,[8] widely investigated for extensive use as a starting material for the construction of larger polyarenes and bowl-shaped fragment of the fullerenes, liquid crystals, and C_3 tripod materials in asymmetric catalysis and chiral recognition.[9]

Up to the present, most of the studies on dendrimers containing acetylene units are that based on phenylacetylene. But there have been few reports of their use in optoelectronic devices, for the planarity of the phenylacetylene-containing dendrimers allows the emissive chromophores to interact strongly in the solid state.[7]

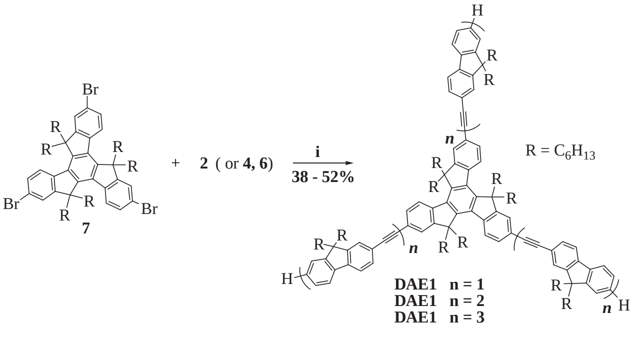
In this paper, we design and synthesize a series of novel monodisperse star-burst oligo(fluoreneethynylene)s, based on the truxene moiety as the core unit, and study their properties preliminary.

To synthesize the target star-burst oligo(fluoreneethynylene)s, our design was to attach oligo(fluoreneethynylene) arms directly to the central core via Sonogashira reaction. Firstly, 2,7,12-tribromo-5,5′,10,10′,15,15′-hexahexyltruxene (**7**) was synthesized as the key intermediate for the whole procedure according to the literature.[10] The compound **7** served as the central core.



Scheme 1. Reagents and conditions: (i) $C_6H_{13}Br$, triethylbenzylammonium chloride, 50% aqueous NaOH, DMSO, rt, 6 h; (ii) I_2, KIO_3, AcOH, H_2SO_4, H_2O, reflux, 8 h; (iii) NBS, $CHCl_3$, rt, 6 h; (iv) $PdCl_2(PPh_3)_2$, CuI, $(CH_3)_3Si(C{\equiv}CH)$, toluene/triethylamine, rt (or 70 °C) 24 h; (v) KOH, THF/CH_3OH, rt; (vi) $PdCl_2(PPh_3)_2$, CuI, toluene/triethylamine, 50 °C, 10 h.

Secondly, oligo(fluoreneethynylene) derivatives **2**, **4**, and **6** were prepared as the other key intermediates to construct the star-bursts, as shown in Scheme 1. In this step, it is more important to generate the moderate-yield intermediates to [2-(9,9-dihexyl-7-iodofluoren-2-yl)ethynyl]trimethylsilane (**1**). In order to get compound **1**, it is vital to control the proportion of the reactants and the reacting temperature to lower the reacting activity of aryl iodide and terminal alkyne. Any of the higher-generation oligo(fluoreneethynylene) were prepared by de-protection of the products coming from the Sonogashira reaction of compound **1** and the lower-generation oligo(fluoreneethynylene). 2,7-Iodo-9,9-dihexylfluorene and 2-ethynyl-9,9-dihexylfluorene were prepared according to the literature.[11] The Sonogashira reaction of compound **1** and 2-ethynyl-9,9-dihexylfluorene (**2**) gave dimeric(fluoreneethynylene) having terminal trimethylsilylethynyl groups in quantitative yield. After deprotection with KOH solution, the dimeric(fluoreneethynylene) **4** was gained. The process was repeated, i.e., the trimeric(fluoreneethynylene) **6** was gained too. The final step to **DAE1**–**DAE3** is outlined in Scheme 2. As shown in Scheme 2, the truxene core was introduced by C–C bond connection at its 2-position with terminal alkynes of oligo(fluoreneethynylene) arms catalyzed by $Pd(PPh_3)_4$/CuI through Sonogashira reaction. As anticipated the products were all efficiently achieved with the



Scheme 2. Reagents and conditions: (i) $Pd(PPh_3)_4$, CuI, toluene/diisopropylamine, 70 °C, 48 h.

Table 1. Physical properties of **DAE1**–**DAE3**

Compound	T_g/T_d (°C)	$\lambda_{abs,max}$/nm		$\lambda_{emi,max}$/nm (λ_{ex}/nm)	
		Solution	Solid Film	Solution	Solid Film
DAE1	187.9/369	354, 375	351,377	384, 401/(375)	447,472/(375)
DAE2	161.5/378	378, 396	380,399	407, 429/(375)	440,466/(380)
DAE3	151.6/388	387, 404	385,406	416, 439/(385)	444,471/(385)

moderate yields. Moreover, all the products show excellent solubility. Noticeably, in this step, it is very sensitive to trifle oxygen, which promotes the coupling of oligo(fluoreneethynylene) to form fluoreneethynylene dimer. The photophysical properties of compounds **DAE1**–**DAE3** were first examined in a diluted chloroform solution (ca. 10^{-5} M). Then, thin films used for fluorescence measurements were obtained by spin-coating chloroform solution (ca. 10 mg/mL) onto quartz plates at 1000 rpm. All compounds exhibited excellent film-forming properties. Photophysical data from both the solution and the solid films are summarized in Table 1.

The thermal stabilities of **DAE**s were determined by thermalgravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen, as shown in Table 1 (or Figure S1 in Supporting Information).[14] It can be observed that the 5% weight-loss temperatures (T_d), with the oligo(fluorene-ethynylene) arms extended, increased from 369 to 388 °C. Noticeably, the T_d of **DAE3** with three repeated fluoreneethynylene units have already higher than the linear poly(fluoreneethynylene) (PFE).[12] In the DSC trace of heating (10 °C/min) up to 250 °C, there are no obvious glass-transition temperature (T_g) observed for the three star-burst compounds. Noticeably, when cooling (−10 °C/min) from 250 °C down to room temperature, their glass-transition temperatures (T_g) were observed to be 187.9, 161.5, and 151.6 °C for **DAE1**, **DAE2**, and **DAE3**, respectively, which greatly higher than the linear PFE.[12]

The UV–vis absorption and fluorescence emission spectra of **DAE1**–**DAE3** are shown in Figure 1. The absorption spectra for compounds **DAE1**–**DAE3** both in solution and in the solid state show two absorption bands, which progressively red-shift with chain length extended. In solution, the short-wavelength peak ranges from 354 to 374 nm; the long-wavelength peak ranges from 375 to 388 nm. With the oligo(fluoreneethynylene) arms extended, the intensity of the short-wavelength peak was strengthened and the interval of two absorption bands was inclined to be fainted. The shapes of the absorption peaks are the same for the chloroform solutions and films. From Figure 1b, the fluorescence emission spectra for **DAE1**–**DAE3** in chloroform solution (1×10^{-5} M) show two absorption bands, which progressively red-shift and increase with chain length extended. In comparison with those in solution, the emission peaks of **DAE1**–**DAE3** in the solid state red-shift markedly (shown in Figure 1d). Such red shifts could be attributed either to the difference in energy-transfer processes between film and solution due to the presence of rotational conformation in the solution reducing the conjugation of the chromophore, or to the effect of packing and local geometry of the DAEs,[13] which is quite common in PAEs materials.[14]

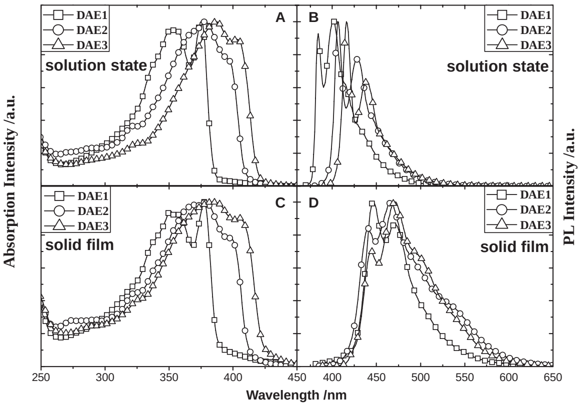


Figure 1. The absorption and fluorescence spectra of **DAE1**–**DAE3** in chloroform solution (1×10^{-5} M) and the solid film.

This work was financially supported by the NSFC under Grants 60578039, 90406021, and 50428303.

References and Notes

1 I. B. Kim, J. N. Wilson, U. H. F. Bunz, *Chem. Commun.* **2005**, 1273; M. D. Disney, J. Zheng, T. M. Swager, P. H. Seeberger, *J. Am. Chem. Soc.* **2004**, *126*, 13343; N. Dicesare, M. R. Pinto, K. S. Schanze, J. R. Lakowicz, *Langmuir* **2002**, *18*, 7785.

2 N. G. Pschirer, T. Miteva, U. Evans, R. S. Roberts, A. R. Marshall, D. Neher, M. L. Myrick, U. H. F. Bunz, *Chem. Mater.* **2001**, *13*, 2691; C. Schmitz, P. Posch, M. Thelakkat, H. W. Schmidt, A. Montali, K. Feldman, P. Smith, C. Weder, *Adv. Funct. Mater.* **2001**, *11*, 41; C. A. Breen, J. R. Tischler, V. Bulovic, T. M. Swager, *Adv. Mater.* **2005**, *17*, 1981.

3 Y. Xu, P. R. Berger, J. N. Wilson, U. H. F. Bunz, *Appl. Phys. Lett.* **2004**, *85*, 4219.

4 U. H. F. Bunz, *Adv. Polym. Sci.* **2005**, *177*, 1; X. Zhao, M. R. Pinto, L. M. Hardison, J. Mwaura, J. Muller, H. Jiang, D. Witker, V. D. Kleiman, J. R. Reynolds, K. S. Schanze, *Macromolecules* **2006**, *39*, 6355.

5 U. H. F. Bunz, J. M. Imhof, R. K. Bly, C. G. Bangcuyo, L. Rozanski, D. A. VandenBout, *Macromolecules* **2005**, *38*, 5892; T. Miteva, L. Palmer, L. Kloppenburg, D. Neher, U. H. F. Bunz, *Macromolecule* **2000**, *33*, 652; C. E. Halkyard, M. E. Rampey, L. Kloppenburg, S. L. Studer-Martinez, U. H. F. Bunz, *Macromolecule* **1998**, *31*, 8655; J. Kim, T. M. Swager, *Nature (London)* **2001**, *411*, 1030.

6 Y. Shirota, *J. Mater. Chem.* **2005**, *15*, 75.

7 S. Lo, P. L. Burn, *Chem. Rev.* **2007**, *107*, 1097.

8 V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klärner, R. D. Miller, D. C. Miller, *Macromolecules* **1999**, *32*, 361.

9 M. M. Boorum, Y. V. Vasil'ev, T. Drewello, L. T. Scott, *Science* **2001**, *294*, 828; A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **2000**, *122*, 6323; T. S. Perora, J. K. Vij, *Adv. Mater.* **1995**, *7*, 919; X.-Y. Cao, W.-B. Zhang, J.-L. Wang, X.-H. Zhou, H. Lu, J. Pei, *J. Am. Chem. Soc.* **2003**, *125*, 12430; J. Pei, J.-L. Wang, X.-Y. Cao, X.-H. Zhou, W.-B. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 9944.

10 A. L. Kanibolotsky, R. Berridge, P. J. Skabara, I. F. Perepichka, D. D. C. Bradle, M. Koeberg, *J. Am. Chem. Soc.* **2004**, *126*, 13695.

11 S. H. Lee, T. Nakamura, T. Tsutsui, *Org. Lett.* **2001**, *3*, 2005.

12 X. Zhan, Y. Liu, G. Yu, X. Wu, D. Zhu, R. Sun, D. Wang, A. J. Epstein, *J. Mater. Chem.* **2001**, *11*, 1606.

13 Y. Kim, S. Kwom, D. Yoo, M. F. Rubner, M. S. Wrighton, *Chem. Mater.* **1997**, *9*, 2699.

14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.: General experimental procedures, ^{1}H and ^{13}C spectra for compounds **1**, **2**, **4**, **6**, and **DAE1**–**DAE3**, and characterization data for all products.

Published on the web (Advance View) January 19, 2008; doi:10.1246/cl.2008.178