Synthesis of Rigid Oligofluorene Stars

Shezhad Jeeva,[a] Stephen C. Moratti*[b]

[a] Liquid Crystal Group, Department of Chemistry, University of York, York, Yorkshire, YO10 5DD, UK

[b] Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand
E-mail: smoratti@chemistry.otago.ac.nz

Received 18 July 2007

Abstract: In this paper we present the synthesis of a tetrahedral oligofluorene-functionalized adamantane, via an iterative synthetic approach, using Suzuki coupling methodology. Tetraphenyladamantane with two fluorene units on each arm were successfully synthesized. These tetrahedral oligofluorene adamantane cores exhibited good optical and thermal properties. One problem in this synthesis of these materials was that the homocoupling of the core became more prevalent as the molecular size increased. This is possibly a common defect in many controlled synthesis of large polyarenes.

Keywords: Pd-coupling, ipso-substitution, conjugation, organometallic reagents, silylation

Conjugated polymers and oiligomers in their pristine states are usually wide-to-medium band-gap semi-conductors.[1] Metallic conductivity can often be induced by doping the polymer with strong oxidants or acids.[2] These materials have a wide range of uses in fields such as light emission, photovoltaics and organic transistors. Control of morphology, such as crystallinity and aggregation is often important for the production of good thin films. One of the most popular synthetic methods with which to synthesize conjugated polymers is Suzuki–Miyaura cross-coupling using palladium catalysis.[3–5]

Since the last decade, tetrahedral organic materials derived from several core compounds such as tetraphenylmethane,[6] tetraphenylsilane,[6b] tetraphenyladamantane,[6b,i,j,7] silsesquioxane[8] and star-shaped porphyrins[9] have attracted much attention. They have been investigated as light-emitting materials, electronically active materials and as a molecular caltrop in scanning probe microscopy.[10] The extended tetrahedral shape of such materials does not allow efficient packing in the solid state and consequently, they tend to form glassy or amorphous states which are ideal for many thin-film technologies such as organic light-emitting diodes (OLEDs). The molecular weights of these oligomers can be quite high and it becomes important to determine the purity and presence of any defects in the structures. Due to the similar and repeating nature of the arms, traditional methods such as NMR, UV/Vis and IR spectroscopy may not be sensitive enough to pick up some defect structures.

SYNTHESIS 2007, No. 21, pp 3323–3328
Advanced online publication: 21.09.2007
DOI: 10.1055/s-2007-990807; Art ID: P08807SS

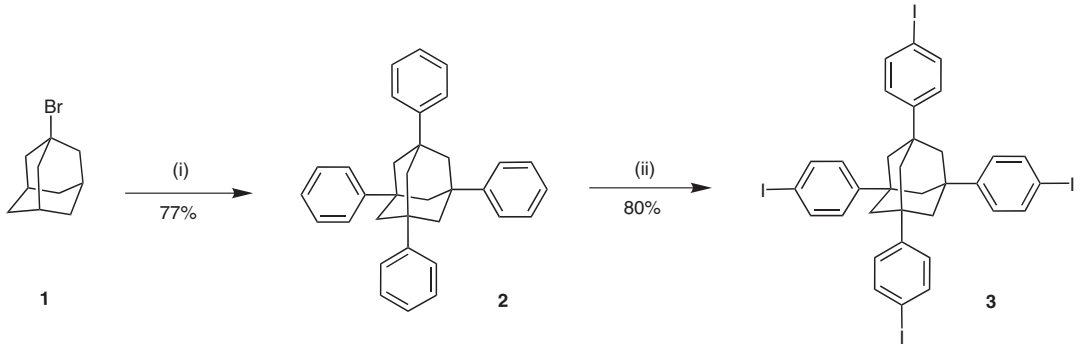
MALDI-TOF mass spectroscopy can be a very useful tool with which to look for defects such as missing end-groups. However, not all impurities might be picked up, especially if they are of much higher molecular weight than expected. Size-exclusion chromatography (SEC) is another important method with which to analyse the purity of such materials. While it is not sensitive enough to find small differences in molecular structure, larger defects such as those arising from dimerisation or a missing arm should be readily seen. Unfortunately, these techniques are not always applied in the analysis of these types of molecules.

To our knowledge, there are very few star-shaped oligofluorene derivatives[10] and the other examples are mostly based on hyperbranched type polymers,[10b] on star-shaped polyphenylene[6h] or on polyphenylene vinylene[6b] oligomers. Unfortunately, no SEC analysis was reported for any of these examples, which would have helped to validate the purity of the materials.

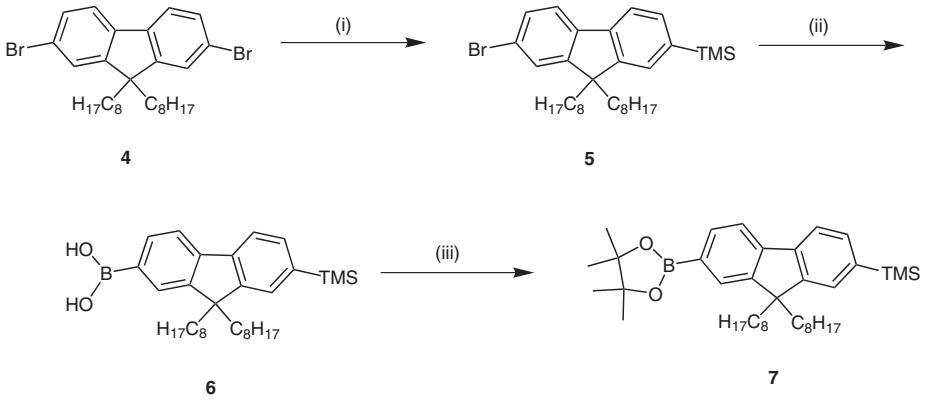
In this paper we present a repetitive divergent synthetic strategy with which to prepare a series of well-defined star-shaped, conjugated oligofluorene derivatives, with tetraphenyladamantane as the core. Adamantane is an ideal nucleus for tetrahedral systems due to its rigid T_d symmetry, all-hydrocarbon nature, and thermal stability.[11] The adamantane core is used here not only to maintain the rigidity but also to give extra core volume, thus disrupting the packing of the tetrahedral stars by its size.[11]

The synthesis of 1,3,5,7-tetrakis(4-iodophenyl)adamantane (**3**) was performed according to literature methods using a Friedel–Crafts reaction followed by iodination (Scheme 1).[11,12]

Initially, the synthesis of a series of unsubstituted polyphenylene arms was attempted. However, solubility was a problem even with the bulky adamantyl core. By using 9,9-disubstituted fluorenyls, the rigidity, stability and blue light emission of polyphenylene systems can be preserved. The iterative syntheses of these types of molecules requires a protection–deprotection strategy similar to those found in dendrimer synthesis. A silyl group was employed here to activate the growing end of the arms. The required monomer **7**, was synthesised in four steps from the known compound **4**. Lithiation and quenching of **4** with trimethylsilyl chloride produced **5** in good yield, which was subsequently transformed into the boronic acid. Since boronate esters are often easier to handle and use than the parent acid, **7** was produced in quantitative



Scheme 1 *Reagent and conditions*: (i) *t*-BuBr, $AlCl_3$, benzene, reflux; (ii) [bis(trifluoroacetoxy)iodo]benzene, I_2.[11]



Scheme 2 *Reagents and conditions*: (i) *n*-BuLi (1.6 M in hexane), –78 °C; TMSCl, –78 °C; (ii) *n*-BuLi (1.6 M in hexane), –78 °C, trimethyl borate, –78 °C; (iii) $MgSO_4$ (anhydrous), MeOH (anhydrous), pinacol, 30 °C.

yield by treatment of **6** with pinacol and used without further purification.[13]

The aim was then to couple the fluorenyl unit to the core and to substitute the silyl group with iodine for subsequent reaction. This method has been previously used to good effect in the iterative synthesis of several large, conjugated molecules. The fluorene units were coupled under Suzuki coupling conditions to the core **3**, in order to increase the arm length (n = 1,2), then the TMS group was substituted with iodine. The structures and purity of the coupled products were investigated by ^1H and ^{13}C NMR, elemental and MALDI-TOF analysis, FT-IR and size exclusion chromatography (SEC).

Thermal and optical properties of the newly synthesised compounds were also investigated. It should be noted that the iodo moieties of the tetrahedral macromolecule were treated as intermediates and, as such, their thermal and optical properties were not investigated due to their lower stability.

The synthesis of compounds **8** and **10** (Figure 1) were carried out via Suzuki coupling as shown in Scheme 2. It was found that the best yields and purity were obtained with $Pd(PPh_3)_4$ as the catalyst and tetraethylammonium hydroxide (20% v/v in H_2O) as the aqueous basic medium with toluene solvent. In order to achieve maximum coupling, the boronic ester **7** was added in excess to the reaction mixture, which was then heated for 24 hours.

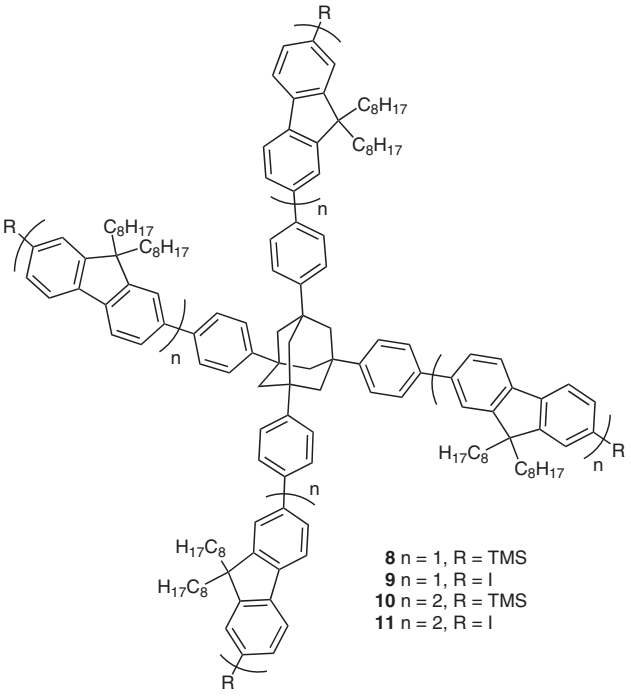


Figure 1

Unfortunately, the progress of the reaction could not be followed by TLC, due to streaking on the plate; for this reason the product could also not easily be purified by col-

umn chromatography. In addition, the similar R_f values of the product and boronic ester precluded their separation.

Therefore, in order to remove the excess of boronic ester **7**, an end-capping technique was used, i.e. an excess of bromobenzene was used to couple with the unreacted boronic ester **7** to form a very nonpolar coupled product which was easily separable from the star. Compound **8** was then eluted using chloroform to give a pale-yellow glassy solid in 60–70% yield. The moderate yield could be due to the fact that compound **8** streaked on silica and was difficult to recover cleanly from the column, even with highly polar solvents.

Iodination of **8** was performed by modifying a standard procedure and is shown in Scheme 3. Standard conditions[14,15] (dropwise addition of ICl in CH_2Cl_2 at 0 °C) gave some unwanted proteo-desilation, which we found could be prevented by the use of solid sodium bicarbonate as an acid scavenger. Aqueous work-up was followed by column chromatography to give a quantitative yield of **9** as a light-red glassy solid. Complete substitution of **9** was confirmed by ^{1}H NMR; the spectra contained neither a TMS peak nor multiplets due to proteo-desilation. The synthesis of compounds **10** and **11** was carried out using similar conditions to those mentioned above for the synthesis of compounds **8** and **9**, respectively.

The ^{1}H and ^{13}C NMR spectra of the compounds **8**–**11** were too complex to definitively confirm the structure. The ^{1}H aromatic region (δ = 7.0–8.0 ppm) was particularly difficult to assign, as the peaks were usually too close to each other to integrate individually; the peaks were therefore considered to be a multiplet. The ^{1}H NMR spectra of these compounds also contain broad peaks with shifts corresponding to the alkyl chains; such peak broadening is common for large molecules due to slow relaxation and inhomogeneity. Elemental analysis and mass spectra data fit the theoretical values, which helps confirm the purity.

SEC was performed in order to check the purity of the compounds **8** and **10** (Figure 2). The molecular weights of both, determined by referencing their retention times to a polystyrene standard, were higher than the expected value from MALDI-TOF measurements. This finding is in qualitative agreement with the general view that rigid-rod macromolecules have a larger hydrodynamic volume than flexible ones of the same molecular weight.[16] The large peak is assumed to be the desired coupled product, while the smaller peak (on the high molecular size side) is believed arise from an impurity which may have formed by the self-coupling of two iodo-cores during the Suzuki coupling reaction. The presence of homo-coupling in these types of reaction has also been previously reported.[17] It was discouraging that the amount of homo-coupling increased with the size of the molecules. Indeed, attempts at a third generation rigid star failed due to excessive side-reactions. The impurity could not be separated by normal chromatography on silica gel due to the very similar polarities. However, preparative SEC on BIORAD biobeads SX-1 gel successfully separated out the first peak in each case.

As can be seen in Figure 3, MALDI-TOF analysis also verified the structure of products **8** (m/z = 2282) and **10** (m/z = 3836). The small fragmentation peak at m/z = 2209.5 in the spectrum of **8** suggests that a TMS group (m/z = 74) was lost, either in the synthesis or under the MALDI analysis conditions. No parent ions could be seen in the MALDI spectra of either iodo-substituted compounds **9** or **11**, probably due to facile loss of iodine.

Thermal gravimetric analysis (TGA) was performed in order to study the potential thermal stability of compounds **8** and **10**. As expected, the compounds proved very stable

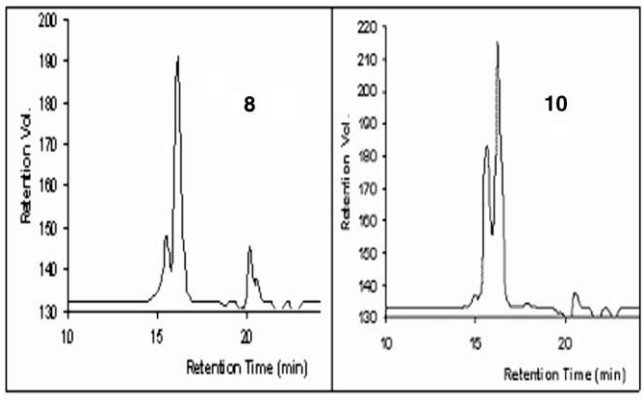
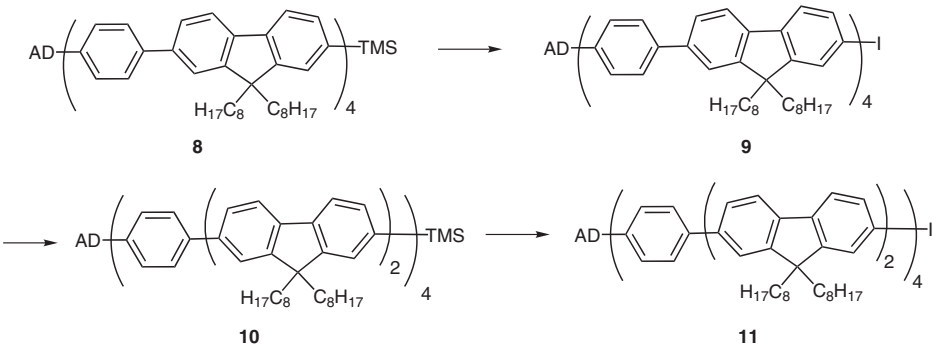


Figure 2 SEC analysis of the crude coupling products before preparative SEC. Peaks around 20 minutes are due to solvent.



Scheme 3 *Reagents and conditions*: (i) $Pd(PPh_3)_4$ (12 mol%), Et_4NOH (20% in H_2O), toluene (degassed, N_2), 90 °C, 24 h; (ii) ICl (1.0 M in CH_2Cl_2), $NaHCO_3$, 0 °C→r.t., overnight. AD = Adamantyl.

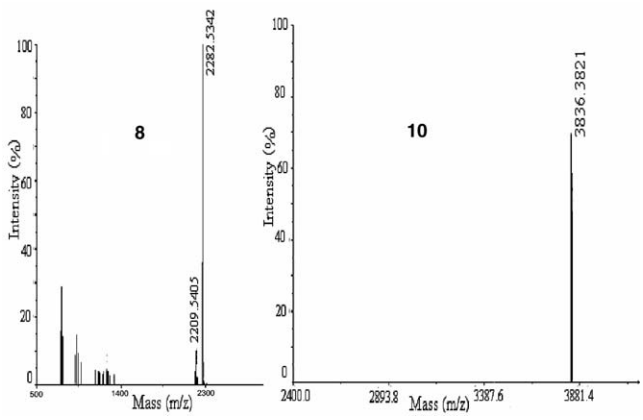


Figure 3 MALDI-TOF spectra of **8** and **10**.

and no loss was seen below 400 °C. Differential scanning calorimetry (DSC) measurements of compounds **8** and **10** exhibited small endothermic peaks on first heating at 99 °C and 170 °C, respectively. However, both failed to give any transitions on cooling or on a second consecutive thermal run; it may be that the first transitions were related to a small amount of trapped solvent, which can be very difficult to remove from these materials.

The UV/Vis absorption of compounds **8** and **10** were measured in THF solution (Table 1). The absorption maximum is red-shifted as the effective conjugated lengths of the respective oligofluorene branches were increased, with **8** and **10** exhibiting maximum absorptions at 328 nm and 350 nm respectively. The UV/Vis spectrum of thin films of compounds **8** and **10** were very similar to those in solution, showing that there was no apparent aggregation or crystallisation in the solid state. These compounds all formed good films upon casting and are thus suitable for opto-electronic applications. The emission maxima are also shown in Table 1. No excimer in the long wavelength emission region of 500–600 nm (typical of polyfluorenes[18–20]), was observed in the solid state. There is some controversy over whether these, often unwanted, emissions are due to aggregation or ketone-type defects.[21]

Table 1 Optical Measurements of Compounds **8** and **10**

Compd	UV_{max} in THF (nm, log ε)	UV (thin film) (nm)	PL (THF) (nm)	PL (thin film) (nm)
8	322 (5.25)	326	344	348
10	350 (5.44)	354	350	354

In summary, a new series of rigid, tetrahedral oligofluorene stars have been synthesized. Palladium-catalysed coupling is shown to give defects due to homo-coupling, which may be a serious limitation to the assembly of multiple arms in the same step. It is important to analyse these types of materials by a wide variety of methods in order to determine the presence of side-reactions. These stars show good thermal stability and form fluorescent, amorphous films.

All reagents were used as received from commercial suppliers, including $Pd(PPh_3)_4$ (Aldrich) and polystyrene (average molecular weight ~280,000 by GC, Aldrich). Moisture-sensitive reactions were conducted in oven- or flame-dried glassware. Temperatures refer to the bath temperature unless specified otherwise. Flash chromatography was performed using Merck 9385 silica gel 60 (0.040–0.063 nm). Yields refer to isolated quantities of analytically pure material unless specified otherwise. FT-IR spectra were measured with Perkin–Elmer Spectrum RX I FT-IR spectrometer. ^1H and ^{13}C NMR were recorded on Bruker DPX-400 (400 MHz) or Bruker DRX-500 (500 MHz) instruments. Elemental analyses were performed with an Exeter Analytical CE-440 elemental analyzer. UV/Vis absorptions were measured using dilute THF solutions in a 1.0 cm path-length quartz cuvette on a Hewlett–Packard 8452A diode array spectrophotometer. Photoluminescence (PL) and excitation spectra were recorded on an Aminco–Bowman Series 2 luminescence spectrometer under an ambient atmosphere. DSC and TGA were performed using a Perkin–Elmer Pyris 1 instrument. SEC was carried out with the aid of a Viscotek Model 200 differential refractometer. MALDI-TOF analysis of the tetrahedral samples were performed on a 4700 proteomics analyzer with TOF/TOF optics (Applied Biosystem); DHB was used as a matrix. GPC = gel-permeation chromatography; PD = polydispersity; M_p = peak molecular weight. The compounds 2,[11,12] 3,[11,12] and 4[22] were prepared as described in the literature.

(7-Bromo-9,9-dioctyl-9*H*-fluorene-2-yl)trimethylsilane (5)[8]

2,7-Dibromo-9,9-dioctyl-9*H*-fluorene (**4**; 17.1 g, 31.2 mmol) was dissolved in anhydrous Et_2O (250 mL) and cooled to –78 °C. *n*-BuLi (21.5 mL; 1.6 M in hexane, 34.3 mmol) was added dropwise via syringe at –78 °C and the mixture was stirred for 3 h at –10 °C. The solution was cooled to –78 °C and TMSCl (5.2 mL, 140.5 mmol) was added dropwise via syringe. The solution was stirred overnight at r.t. then H_2O (100 mL) was added to quench the reaction. The organic layer was taken, washed with H_2O (2 × 200 mL) and the mixture was dried ($MgSO_4$) and evaporated to give the product **5**. Yield: 17.5 g (95%); pale-yellow oil.

IR (neat): 3039, 2956, 2929, 2884, 2857, 1600–1471, 1248 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 6.2 Hz, 1 H), 7.57 (d, *J* = 7.9 Hz, 1 H), 7.46 (m, 4 H), 1.84 (m, 4 H), 1.35 (m, 20 H), 0.82 (t, *J* = 5.0 Hz, 6 H), 0.61 (m, 4 H), 0.31 (s, 9 H).

2-(9,9-Dioctyl-7-trimethylsilanyl-9*H*-fluoren-2-yl)boronic Acid (6)[8]

7-Bromo-9,9-dioctyl-9*H*-fluorene-2-yl)trimethylsilane (**5**; 9 g, 16.4 mmol) was dissolved in anhydrous THF (100 mL) and cooled to –78 °C. *t*-BuLi (20 mL, 1.7 M in pentane, 34.5 mmol) was added dropwise via syringe (the colour of the reaction mixture changed from yellow to dark green) and the mixture was stirred for 3 h at –78 °C. $(i\text{-PrO})_3B$ (11 mL, 49.9 mmol) was added and the mixture was stirred overnight at r.t. under an atmosphere of N_2. H_2O (40 mL) was added to quench the reaction and the organic layer was separated and washed with H_2O (2 × 200 mL). The organic layer was dried ($MgSO_4$) and evaporated to give **6**. Yield: 5.2 g (61%); pale-yellow oil.

^1H NMR of the product was complex due to dimer and trimer formation.

IR (ATR): 3549, 3027, 2951, 2921, 2855, 1608–1416, 1352, 1246 cm^{-1}.

2-(9,9-Dioctyl-7-trimethylsilanyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)[8]

To a solution of 2-(9,9-dioctyl-7-trimethylsilanyl-9*H*-fluoren-2-yl)boronic acid (**6**; 5 g, 10 mmol) in anhydrous MeOH (100 mL), was added anhydrous $MgSO_4$ (5 g) followed by pinacol (5 g, 40 mmol). The mixture was stirred at 30 °C for 24 h then cooled to r.t.

and EtOAc (100 mL) was added followed by H_2O (200 mL). After stirring for 10 min, the organic layer was separated, dried ($MgSO_4$), filtered and then evaporated under reduced pressure to give a pale-yellow sticky solid (6.5 g, 80%) that was recrystallized (Et_2O–MeOH, 1:5) to give pure **7**. Yield: 5.2 g, 52%; pale-yellow crystals; mp 72–73 °C.

IR (ATR): 3027, 2951, 2921, 2855, 1608–1416, 1352, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.69 (m, 4 H), 7.47 (m, 2 H), 1.97 (m, 4 H), 1.39 (s, 12 H, CH_3CO), 1.21–1.03 (m, 20 H, CH_2), 0.81 (t, J = 7.0 Hz, 6 H), 0.55 (m, 4 H, CH_2), 0.31 (s, 9 H).

Suzuki Coupling; General Procedure

Arylhalide (0.9 mmol), arylboronic ester (5.5 mmol) and $Pd(PPh_3)_4$ (12.0 mol%) dissolved in toluene (50 mL, degassed) were placed in a one-neck round-bottom flask (250 mL). Et_4NOH (25 mL) was added and the system was degassed and stirred at 85 °C under an atmosphere of N_2 overnight. The system was cooled to r.t. and a solution of PhBr (excess, 100 mg), $Pd(PPh_3)_4$ (10 mg) and Et_4NOH (2.0 mL) dissolved in toluene (5.0 mL) was added via syringe. The system was degassed again and heated at 85 °C under the atmosphere of N_2 for 24 h. After cooling to r.t., toluene (50 mL) was added followed by H_2O (200 mL).

1,3,5,7-Tetrakis[(9,9-dioctyl-7-phenyl-9*H*-fluoren-2yl)trimethylsilane]adamantane (8)

According to the general procedure described above. The organic layer was separated, dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude yellow glassy product that was purified by column chromatography (hexane then $CHCl_3$–hexane, 1:4) to give **8**. Yield: 1.2 g (60%); colourless glassy solid.

IR (ATR): 3027, 2951, 2921, 2850, 1600–1464, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.46 (m, 40 H), 2.30 (s, 52 H), 1.99 (m, 16 H), 1.21–1.08 (m, 40 H), 0.81 (t, J = 5.0 Hz, 24 H), 0.78–0.70 (m, 16 H), 0.31 (s, 36 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5, 150.1, 148.2, 141.3, 140.2, 139.6, 138.9, 119.9, 118.9, 55.0, 47.4, 40.2, 39.1, 31.7, 29.9, 29.1, 29.0, 23.7, 22.5, 14.0, –0.9.

MS (MALDI-TOF): m/z [$C_{162}H_{224}Si_4$] = 2282.5842.

Anal. Calcd for $C_{162}H_{224}Si_4$: C, 85.20; H, 9.89. Found: C, 85.48; H, 9.70.

UV/Vis (THF): λ_{max} (ε) = 322 (1.78×10^5) nm.

UV/Vis (thin film): λ_{max} = 326 nm.

PL (THF): $\lambda_{emission}$ = 344 nm.

DSC: T_c 92 °C, T_m 99 °C; TGA decomposition events seen at 423 °C and 639 °C.

GPC (THF): PD = 1.14, M_p = 2990.

1,3,5,7-Tetrakis[7-phenyl-bis(9,9-dioctyl-9*H*-fluoren-2-yl)trimethylsilane]adamantane (10)

According to the general procedure described above. The organic layer was separated, dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude yellow glassy product. Purification by column chromatography ($CHCl_3$–hexane, 1:20 then $CHCl_3$) gave a light-brown glassy product (939 mg, 70% crude yield). A sample (110 mg) was then subject to preparative SEC using BIO-RAD SX-1 biobeads (CH_2Cl_2) to give **10** (56 mg).

IR (ATR): 3022, 2951, 2926, 2855, 1600–1400, 1246 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.48 (m, 64 H), 2.37 (s, 12 H), 2.16–1.99 (m, 32 H), 1.24–0.87 (m, 80 H), 0.84–0.73 (m, 48 H), 0.32 (s, 36 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.7, 151.6, 150.2, 148.0, 140.55, 140.50, 140.3, 140.2, 140.0, 139.9, 139.6, 139.5, 138.1, 131.7, 128.1, 127.6, 127.2, 126.0, 125.98, 125.91, 125.55, 121.50, 121.44, 121.40, 119.96, 119.91, 118.0, 55.2, 55.0, 47.1, 40.3, 40.1, 39.6, 31.9, 30.1, 29.9, 29.6, 29.2, 29.19, 29.13, 29.08, 14.1, –0.86.

MS (MALDI-TOF): m/z ($C_{278}H_{384}Si_4$) = 3838.37.

Anal. Calcd for $C_{278}H_{384}Si_4$: C, 86.45; H, 9.92. Found: C, 86.99; H, 10.08.

UV/Vis (THF): λ_{max} (ε) = 348 (1.95×10^5) nm.

UV/Vis (thin film): λ_{max} = 348 nm.

PL (THF): $\lambda_{emission}$ = 406 nm, thin film 409 nm, doped with Ir(acac) complex (127) 568 nm.

DSC: T_c = 130 °C, T_m = 170 °C; TGA decomposition events seen at 304, 450, 568 °C.

GPC (THF): PD = 1.09, M_p = 5540.

1,3,5,7-Tetrakis(7-phenyl-2-iodo-9,9-dioctyl-9*H*-fluorene)adamantane (9)

1,3,5,7-Tetrakis[(9,9-dioctyl-7-phenyl-9*H*-fluoren-2-yl)trimethylsilane]adamantane (**8**; 400 mg, 0.2 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) in a dry one-neck round-bottom flask (100 mL). $NaHCO_3$ (1 g) was added and the mixture was stirred at –10 °C then iodomonochloride (1.0 M in CH_2Cl_2, 1 mL, 1.05 mmol) was added dropwise and the mixture was stirred at r.t. for 12 h under an atmosphere of N_2. The reaction mixture was quenched by adding aqueous $Na_2S_2O_3$ (2.0 M, 50 mL) and stirred until the pink colour of the reaction mixture became colourless. The reaction mixture was poured into a conical flask and CH_2Cl_2 (100 mL) was added followed by H_2O (100 mL). The organic layer was extracted, dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a red solid that was dissolved in CH_2Cl_2 and passed through a plug of silica to remove colour. Evaporation of the solvent gave **9**. Yield: 440 (100%); colourless glassy solid.

IR (ATR): 3027, 2951, 2921, 2855, 1519–1456 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.44 (m, 40 H), 2.3 (s, 12 H), 2.03–1.89 (m, 16 H), 1.24–0.99 (m, 40 H), 0.79 (t, J = 5.3 Hz, 24 H), 0.72–0.57 (m, 16 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3, 150.8, 148.4, 140.3, 140.2, 139.4, 139.3, 135.8, 132.0, 127.1, 126.0, 125.5, 121.4, 121.3, 120.0, 55.3, 47.4, 40.2, 39.2, 31.7, 29.9, 29.1, 23.6, 22.5, 14.0.

MS (MALDI-TOF): m/z = 2496.76.

UV/Vis (THF): λ_{max} (ε) = 326 (1.62×10^5) nm.

UV/Vis (thin film): λ_{max} = 334 nm.

PL (THF): $\lambda_{emission}$ = 346 nm.

GPC (THF): PD = 1.09, M_p = 3000.

1,3,5,7-Tetrakis(bis-7-phenyl-2-iodo-9,9,-dioctyl-9*H*-fluorene)adamantane (11)

In a dry one-neck round-bottom flask (100 mL), 1,3,5,7-tetrakis[7-phenyl-bis(9,9-dioctyl-9*H*-fluoren-2-yl)trimethylsilane]adamantane (**10**; 1.2 g, 0.3 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL). $NaHCO_3$ (1.0 g) was added and the mixture was stirred at –10 °C. Iodomonochloride (1.5 mL, 1.0 M in CH_2Cl_2, 1.5 mmol) was added dropwise and the mixture was stirred at r.t. for 12 h under an atmosphere of N_2. The reaction mixture was quenched by adding aqueous $Na_2S_2O_3$ (2.0 M, 50 mL) and stirred until the pink colour of the reaction mixture became colourless. The reaction mixture was poured into a conical flask and CH_2Cl_2 (100 mL) was added followed by H_2O (100 mL). The organic layer was separated, dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a red glassy compound. The crude material was purified by column chromatography (hexane–CH_2Cl_2, 20:1) to give **11**. Yield: 0.5 (42%); transparent glassy product.

IR (ATR): 3027, 2951, 2921, 2855, 1519–1456 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.63 (m, 64 H), 2.3 (s, 12 H), 2.03–1.89 (m, 32 H), 1.24–0.99 (m, 80 H), 0.79–0.57 (m, 48 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4, 150.8, 148.3, 140.3, 140.2, 139.4, 135.8, 132.0, 127.2, 126.2, 125.9, 121.4, 121.3, 120.0, 55.1, 47.8, 40.0, 39.1, 31.2, 29.9, 29.1, 23.4, 22.1, 14.1.

GPC (THF): PD = 1.25, M_p = 5060.

Acknowledgment

We acknowledge the Aga Khan Foundation for a scholarship (S.J.).

References

(1) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(2) Ching, C. K.; Fincher, C. R. Jr.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.
(3) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.
(4) Oh-e, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, *58*, 2201.
(5) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213.
(6) (a) Constable, E. C.; Eich, O.; Housecrost, C. E.; Johnston, L. A. *Chem. Commun.* **1998**, 2661. (b) Wang, S.; Oldham, W. J. Jr.; Hudack, R. A. Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695. (c) Sengupta, S.; Pal, N. *Tetrahedron Lett.* **2002**, *43*, 3517. (d) Sengupta, S.; Purkayastha, P. *Org. Biomol. Chem.* **2003**, *1*, 436. (e) Sengupta, S.; Sadhukhan, S. K. *Tetrahedron Lett.* **2001**, *42*, 3659. (f) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Lett.* **2001**, *3*, 2887. (g) Sengupta, S.; Sadhukhan, S. K.; Muhuri, S. *Tetrahedron Lett.* **2002**, *43*, 3521. (h) Wilson, L. M.; Griffin, A. C. *J. Mater. Chem.* **1993**, *3*, 991. (i) Li, Q.; Rukavishnikov, A. V.; Petukhov, P. A.; Zaikova, T. O.; Keana, J. F. W. *Org. Lett.* **2002**, *4*, 3631. (j) Li, Q.; Rukavishnikov, A. V.; Petukhov, P. A.; Zaikova, T. O.; Jin, C.; Keana, J. F. W. *J. Org. Chem.* **2003**, *68*, 4862. (k) Yeh, H.-C.; Lee, R.-H.; Chan, L. H.; Lin, T.-Y. J.; Chen, C.-T.; Balasubramaniam, E.; Tao, Y.-T. *Chem. Mater.* **2001**, *13*, 2788.
(7) Li, Q.; Jin, C.; Petukhov, P. A.; Rukavishnikov, A. V.; Zaikova, T. O.; Phadke, A.; LaMunyon, D. H.; Lee, M. D.; Keana, J. F. W. *J. Org. Chem.* **2004**, *69*, 1010.
(8) Lin, W.-J.; Chen, W.-C.; Wu, W.-C.; Niu, Y.-H.; Jen, A. K.-Y. *Macromol.* **2004**, *37*, 2335.
(9) Li, B.; Li, J.; Fu, Y.; Bo, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3430.
(10) (a) Liu, X.-M.; Chaobin He; Huang, J.; Xu, J. *Chem. Mater.* **2005**, *17*, 434. (b) Liu, X.-M.; Chaobin He; Hao, X.-T.; Tan, L.-W.; Li, Y.; Ong, K. S. *Macromol.* **2005**, *37*, 5965. (c) Han, Y.; Fei, Z.; Sun, M.; Bo, Z.; Liang, W.-Z. *Macromol. Rapid Commun.* **2007**, *28*, 1017.
(11) Reichert, V. R.; Mathias, L. J. *Macromol.* **1994**, *27*, 7015.
(12) Li, Q.; Rukavishnikov, A. V.; Petukhov, P. A.; Zaikova, T. O.; Jin, C.; Keana, J. F. W. *J. Org. Chem.* **2003**, *68*, 4862.
(13) Geng, Y.; Trajkovska, A.; Karsus, D.; Ou, J. J.; Culligan, S. W.; Chen, S. H. *J. Am. Chem. Soc.* **2002**, *124*, 8337.
(14) Liess, P.; Hensel, V.; Schlüter, A.-D. *Liebigs Ann.* **1996**, 1037.
(15) Hensel, V.; Schlüter, A.-D. *Liebigs Ann./Recl.* **1997**, 303.
(16) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulz, M.; Köhler, W.; Wegner, G. *Macromol.* **1996**, *29*, 5136.
(17) (a) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6361. (b) Van Asselt, R.; Elsevier, C. J. *Organometallics* **1994**, *13*, 1972. (c) Catellain, M.; Motti, E.; Minari, M. *Chem. Commun.* **2000**, 158.
(18) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477.
(19) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365.
(20) Gong, X.; Lyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S. *Adv. Funct. Mater.* **2003**, *13*, 325.
(21) (a) Lu, H.-H.; Liu, C.-Y.; Jen, T.-H.; Liao, J.-L.; Tseng, H.-E.; Huang, C.-W.; Hung, M.-C.; Chen, S.-A. *Macromolecules* **2005**, *38*, 10829. (b) Becker, K.; Lupton, J. M.; Feldmann, J.; Nehls, B. S.; Galbrecht, F.; Gao, D. Q.; Scherf, U. *Adv. Funct. Mater.* **2006**, *16*, 364.
(22) Ranger, M.; Leclerc, M. *Can. J. Chem.* **1998**, *76*, 1571.